

Development of [60] fullerene supported on silica catalysts for the photo-oxidation of alkenes

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ABSTRACT

Simple or successive incipient wetness impregnation followed by heating at 180 °C is proved an efficient preparation method for dispersing effectively onto the silica surface various amounts of C₆₀ in the range 1–4% (w/w). BET, XRD, DRS, TGA, microelectrophoresis and photoluminescence have been used to characterize the photocatalysts prepared. A high dispersion was obtained for the quite stable supported C₆₀ phase, comprised mainly from relatively small or medium size C₆₀ clusters/aggregates. The photocatalytic activity was assessed in the singlet oxygen oxidation of alkenes by examining the photo-oxygenation of 2-methyl-2-heptene as a probe reaction. The catalytic tests were carried out at 0–5 °C in CH₃CN, under oxygen atmosphere and using a 300 W xenon lamp as the light source. The heterogeneous catalysts obtained were proved to be active in the photocatalytic oxidation of olefins via a ¹O₂ ene reaction. The catalysts exhibited significant conversion, turnover number and turnover frequency values, substantially higher than those achieved over the unsupported C₆₀. The conversion increases with the amount of the supported C₆₀ up to a value equal to 3% (w/w) and then it decreases whereas turnover number and turnover frequency decreases monotonically as the amount of the supported C₆₀ increases. The easy separation of these solid catalysts from the reaction mixture, the high activity and stability as well as the retained activity in subsequent catalytic cycles, make these supported catalysts suitable for a small-scale synthesis of fine chemicals.

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1. Introduction

Oxidation is one of the most fundamental reactions in organic synthesis. Among the several oxidation protocols reported so far, the photo-oxidation with singlet oxygen possesses a rather prominent role [1–3]. Singlet oxygen (¹O₂) is the first excited state of triplet, ground state oxygen, and it is frequently used in organic synthesis because of its highly selective reaction with olefins according to the Schenck 'ene' reaction [4,5]:

The hydroperoxide formed in this reaction is usually immediately reduced to the corresponding allylic alcohol. This route is a unique way to functionalize in one step an unsaturated hydrocarbon and prepare allylic alcohols that cannot be prepared easily

via other routes. Allylic alcohol derivatives are valuable products or key intermediates in the synthesis of fine chemicals.

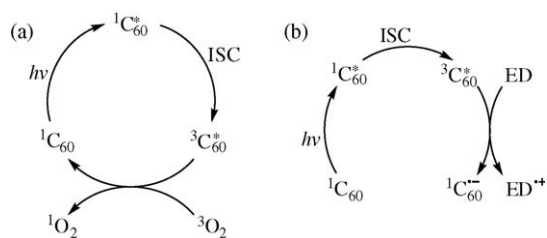
In the numerous synthetic applications of ¹O₂ that have been published so far, ¹O₂ is usually formed by photo-excitation, using various photosensitizers such as methylene blue (MB), rose bengal (RB), porphyrines, and fullerenes [1–8]. In these oxidation reactions an environmentally friendly reagent, such as molecular oxygen, is used at room temperature and atmospheric pressure. However, a further step in the development of environmentally benign oxidation processes requires the replacement of the current homogeneous procedures with heterogeneous processes that comprise the use of a solid, recoverable catalyst. One way to attain this goal is to immobilize one or more components of the active catalyst onto a large surface area of a solid carrier. Immobilized catalysts have recently attracted great interest due to several advantages, such as simplified product workup, separation, isolation, and catalyst reuse.

A key property of a photosensitizer is the quantum yield of singlet oxygen (Φ_{Δ}) which is defined as the number of ¹O₂

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Scheme 1. Photochemical pathways of C_{60} upon light excitation: (a) energy-transfer and (b) electron-transfer.

generated per number of photons absorbed. Fullerenes are excellent singlet oxygen sensitizers with a 1O_2 quantum yield approaching unity. [60] Fullerene absorbs strongly in the UV and moderately in the visible regions of the spectrum [9–11]. The singlet excited state of C_{60} ($^1C_{60}^*$), initially formed upon light excitation, undergoes intersystem crossing (ISC) to the much longer lived triplet excited state ($^3C_{60}^*$) that can be efficiently quenched by molecular oxygen, through a triplet energy transfer, to generate large amounts of the reactive singlet oxygen (*type II* energy-transfer pathway (Scheme 1a) [12–14]. On the other hand, the excited triplet state of fullerene is an excellent electron acceptor, and the reduced fullerene triplet ($^3C_{60}^-$) is formed rapidly in the presence of electron donors (ED) (*type I* electron-transfer pathway, Scheme 1b) [15,16]; this radical species may react further (e.g., through radical coupling with other organic radicals) [17,18].

Silica and γ -alumina are the most important carriers in the heterogeneous catalysis exhibiting very high specific surface area, mechanical and thermal stability. Moreover, these are in principle photocatalytically inert. Therefore, these are suitable materials for mounting C_{60} and studying its photocatalytic behaviour for the aforementioned model reaction.

In the present paper, further developing our interest in heterogeneous photocatalysis [19–21], we report on the preparation and characterization of a series of SiO_2 -supported fullerene catalysts with varying C_{60} content by studying the nature, the state of dispersion and the stability of the C_{60} phase against sublimation/combustion. Moreover, we explore the stability, reusability, and activity of these catalytic systems in the 1O_2 oxidation of alkenes (*type II* pathway), examining the 2-methyl-2-heptene oxidation as a model reaction.

2. Experimental

2.1. Preparation of the silica-supported photocatalysts

A series of supported $C_{60}(x)$ photocatalysts of varying C_{60} content was prepared by depositing C_{60} on the surface of silica grains. Silica [Alfa Aesar, silicon(IV) oxide amorphous fumed, 99.8% metal base, specific surface area $226\text{ m}^2/\text{g}$, specific pore volume 1.6 mL/g and solid C_{60} [Ses Research] have been used. The x in the aforementioned notation denotes the C_{60} content of the photocatalyst (C_{60} , % w/w). It takes the values 1, 2, 3 and 4. These nominal values were confirmed experimentally by determining the carbon content using a Carlo Erba CHN analyzer (EA 1108, Elemental Analyzer).

The samples with $x = 1$ and 2 were prepared by simple incipient wetness impregnation. The impregnating solution was prepared by dissolving the proper amount of C_{60} in 1,2-dichlorobenzene in order to be obtained the desired loading in the final catalysts. The impregnated samples were dried at $180\text{ }^\circ\text{C}$ for 4 h in air. The samples with $x = 3$ and $x = 4$ were prepared starting from the sample with $x = 2$ following the same impregnation procedure described above.

2.2. Characterization of the silica-supported photocatalysts

2.2.1. Specific surface area measurements (SSA)

The BET-SSA of the samples was determined following a flow technique and using a laboratory-constructed apparatus. Pure nitrogen (Linde special) and helium (Linde 99.996%) were used as adsorbate and inert gas, respectively. The amount of nitrogen adsorbed at liquid-nitrogen temperature and at three different partial pressures was determined using a thermal conductivity detector of a gas chromatograph (Varian Series 1700).

2.2.2. X-ray powder diffraction (XRD)

The XRD patterns of the powdered samples were recorded with an ENRAF NONIOUS FR 590 diffractometer. A $Cu\ K\alpha$ (1.54198 \AA) radiation has been used. The generator was equipped with a curved position sensitive detector CPS120 of INEL. This was operated at 45 kV and 25 mA.

2.2.3. Diffuse reflectance spectroscopy (DRS)

The diffuse reflectance spectra of the heated samples were recorded at room temperature in the range 200–800 nm using a UV-vis spectrophotometer (Varian Cary 3) equipped with an integration sphere. Silica was used as reference. The powdered samples were mounted in a quartz cell. This provided a sample thickness greater than 3 mm to guarantee the “infinite” sample thickness.

2.2.4. Photoluminescence

The photoluminescence spectra of the silica and silica-supported photocatalysts were recorded at room temperature in air. A Shimadzu RF-5301 spectrofluorophotometer has been used. This was equipped with a 150 W xenon lamp, a red sensitive photomultiplier and reflection grating monochromators with fixed slits of 3 nm. The wavelength accuracy was $\pm 1.5\text{ nm}$. A long-wavelength passing filter (UV-35) was used on the emission monochromator side to cut off the scattered and the second-order lights.

2.2.5. Microelectrophoresis

The ζ potential of the solid particles was measured using a Zetasizer 5000 (Malvern Instruments Ltd.) microelectrophoresis apparatus. The measurements were carried out at $25\text{ }^\circ\text{C}$. Sufficiently dilute aqueous suspensions of a given sample were prepared with ionic strength equal to 0.01 M. The pH of the suspensions was adjusted by small additions of a 1 M HNO_3 or KOH solution. The ‘ ζ potential vs. pH’ curves were thus obtained. The pH value at which the ζ potential takes a zero value is identified as the isoelectric point of the sample (IEP).

2.2.6. Fourier transform infrared spectroscopy (FT-IR)

Infrared spectra were recorded in the range $400\text{--}4400\text{ cm}^{-1}$, with a nominal resolution of 2 cm^{-1} and averaging 10 spectra. All samples were prepared as KBr pellets and analyzed on a PerkinElmer 16 PC FT-IR spectrophotometer.

2.2.7. Thermogravimetric analysis (TGA)

The TGA of the samples was carried out in a He atmosphere. A DuPont thermo-balance has been used. In all experiments the sample temperature was increased from 25 to $700\text{ }^\circ\text{C}$ using a heating rate of $10\text{ }^\circ\text{C min}^{-1}$.

2.2.8. C_{60} extraction experiments

C_{60} extraction experiments have been performed by immersing a given amount of each catalyst for over 4300 min in a volume of 1,2-dichlorobenzene fifteen times greater than the pore volume of the sample.

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