Fullerene C_{60} supported on silica and γ-alumina catalyzed photooxidations of alkenes

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Deposition of fullerene C_{60} (2% w/w) on silica and γ-alumina provokes a two orders-of-magnitude increase of its activity for the liquid-phase photooxidation of 2-methyl-2-heptene. Kinetic studies concerning the above photooxidation showed a first-order dependence of the reaction rate on the alkene concentration. The corresponding reaction-rate constant was found to be higher in the case where γ-alumina was used as carrier. The nature of the carrier does not influence the mechanism and the selectivity of the reaction. High dispersion of the supported fullerene is achieved on the surface of the carriers, which increase the fullerene light absorbance especially in the visible range.

KEY WORDS: fullerene; C_{60}; photooxidation; alkene photooxidation; support; Al_2O_3; SiO_2; kinetics.

1. Introduction

Six years after the discovery of fullerenes, by Kroto and coworkers [1], Foote and coworkers [2,3] carried out the first investigations of their basic photophysical properties. The fact that the fullerene C_{60} shows strong absorption bands in the ultraviolet ($\varepsilon_{max} \sim 10^5\,M^{-1}\,cm^{-1}$; $\lambda_{max} = 211, 256, 328\,nm$) and weaker in the visible region ($\varepsilon_{max} \sim 710\,M^{-1}\,cm^{-1}$; $\lambda_{max} = 540\,nm$), makes possible the use of different wavelengths for excitation to its singlet state (S_1). However, due to the short singlet lifetime and the efficient intersystem crossing (ISC), the triplet state (T_1) is formed nearly quantitatively. The triplet state of C_{60}, in solution, has a lifetime between 40 and 280 μs [4,5]. In the presence of oxygen, energy transfer takes place from the triplet state of C_{60} to the ground state of oxygen, with quantum yield near unity, providing singlet molecular oxygen ($^1O_2$). Singlet oxygen can oxidize a series of unsaturated substrates [6–9], and its lifetime in solution varies between μs and ms depending on the solvent [10]. In addition, it is known that fullerenes are easily reduced and that quenching of their triplet-excited states by electron donors occurs efficiently in polar solvents. This is achieved by an electron-transfer mechanism [11–13]. The use of C_{60}, as a photosensitizer in solution, has already been reported [14–16].

Supported photosensitizer used as a suspension in a liquid reaction mixture [17], offer many advantages such as ease of photoproduct separation, recycling of the sensitizer, and circumventing a poor solubility of the photocatalyst in the reaction medium.

In the present work, we report on the preparation of fullerene C_{60} supported on silica (C_{60}/SiO_2) and alumina (C_{60}/Al_2O_3), and we compare the catalytic photoactivity of the unsupported fullerene to that of fullerene supported on the two carriers for the liquid-phase photooxidation of 2-methyl-2-heptene.

2. Experimental

Supported photosensitizers were prepared by depositing C_{60} on γ-Al_2O_3 (Akzo, specific surface area: $231\,m^2\,g^{-1}$, size: 100–150 mesh powder, pore volume: $0.76\,mL\,g^{-1}$) and SiO_2 (Alfa Aesar, specific surface area: $226\,m^2\,g^{-1}$, size: ~325 mesh powder, pore volume: $1.6\,mL\,g^{-1}$) surfaces. Incipient wetness impregnation was used for the above deposition. The impregnating solution was prepared by dissolving the necessary amount of C_{60} [Ses Research] in 1,2-dichloro-benzene in order that a loading of 2% w/w C_{60} be achieved in the final catalysts. The impregnated samples were dried at 180 °C for 4 h in air. Impregnated and/or final (dried) samples were characterized using UV-Vis diffuse reflectance spectroscopy (Varian, Cary 3), nitrogen physisorption for specific surface area measurements, and carbon analysis (Carlo Erba Instrument CHN EA 1108, Elemental Analyzer). Experimental details for these characterization techniques have been given elsewhere [18,19].

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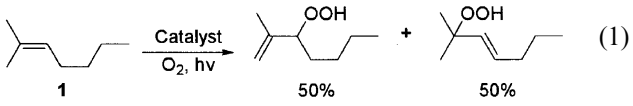
The photooxidation tests were carried out in a 4 mL pyrex semi-batch microreactor at 0 °C by bubbling dry oxygen. The reaction mixture was constituted by 1 mL of CH_3CN, 3.6 mg of the catalyst (C_{60}/Al_2O_3 or C_{60}/SiO_2, $\sim 10^{-4}$M in C_{60}), 3.36 mg of 2-methyl-2-heptene (**1**) (2-methyl-2-heptene was prepared in 68% yield by Wittig coupling of isopropyltriphenylphosphorane with pentanal and purified by vacuum distillation. ^{1}H NMR: δ 0.91 (m, 3H), 1.32 (m, 4H), 1.62 (s, 3H), 1.71 (s, 1H), 1.99 (m, 2H), 5.14 (t, 1H); ^{13}C NMR: δ 14.34, 17.92, 22.78, 26.02, 28.15, 32.54, 125.31, 131.39; MS: m/e 112 (M^+), 97, 83, 69 (100), 56, 41.) (0.03 M) and 5 μL *n*-nonane as internal standard. A Varian-Eimac Cermax 300-W xenon lamp was used as the light source, with a Pyrex filter. Aliquots of the reaction mixture were pooled out and analyzed by GC-MS on a Supelco capillary column (SPB-5, 30 m) in a Shimatzu GCMS-QP5050 (CI mass detector), after reduction of the hydroperoxide products by triphenylphosphine. Two photooxidation tests were performed with unsupported C_{60}. The first of them was carried out using 3.6 mg of C_{60} and the second using the same amount of C_{60} with that used in the case of the supported catalysts (10^{-4} M C_{60} in the reaction mixture).

3. Results and discussion

Photooxidation of 2-methyl-2-heptene proceeds via a singlet oxygen alkene ene reaction producing quantitatively the corresponding allylic hydroperoxides (equation 1).



(1)

The molar ratio of the produced allylic hydroperoxides is independent of the photocatalyst. We have also shown previously that photooxidation of trimethylene in solution, with a variety of sensitizers such as fullerene C_{60}, rosebengal (RB) and tetraphenylporphyrine (TPP), proceeds via singlet oxygen mechanism [14]. The present results suggest that the deposition of the C_{60} on the surface of γ-Al_2O_3 and SiO_2 does not change the reaction mechanism.

Table 1 compiles the conversions of the 2-methyl-2-heptene achieved over the carriers, the unsupported C_{60}, and the supported C_{60} samples after irradiation of the reaction mixture for 150 min. Negligible conversions were achieved without any solid or over the carriers. The most important observation is that the deposition of C_{60} on the surface of the carriers increases dramatically the catalytic activity for the photooxidation of 2-methyl-2-heptene.

To obtain more information on the photocatalytic efficiency of these carriers, we studied the formal kinetics of the photooxidation of **1**. Considering that during the catalytic photooxidations the oxygen concentration in the reaction mixture remained constant and assuming a first-order dependence of reaction rate on the alkene concentration, the following equation can be written:

$$k \cdot t = -\ln(1 - x) \quad (2)$$

where k, t, and x represent the reaction-rate constant, the reaction time and the conversion of alkene, respectively. According to equation (2), the values of its right-hand side should be changed linearly with time. Figure 1 shows that this is, indeed, the case, thus confirming the aforementioned assumptions and indicating that the C_{60} deposition does not cause any change in the reaction kinetics.

The values of the reaction-rate constants achieved over unsupported and supported C_{60} catalysts were calculated by the slopes of the corresponding straight

Table 1
The conversions (x) of 2-methyl-2-heptene measured at 0 °C after irradiation of the reaction mixture for 150 min without any photocatalyst, over the carriers as well as over the unsupported and supported C_{60}

Solid used as photocatalyst[a]	x
No solid	0.004
SiO_2	0.030
Al_2O_3	0.060
C_{60}	0.180
C_{60}/SiO_2	1.000
C_{60}/Al_2O_3	1.000

[a] 3.6 mg of solids were used in all cases with the exception of unsupported fullerene, the concentration of which in the reaction mixture was 10^{-4} M, corresponding to that involved in the suspension of the supported samples.

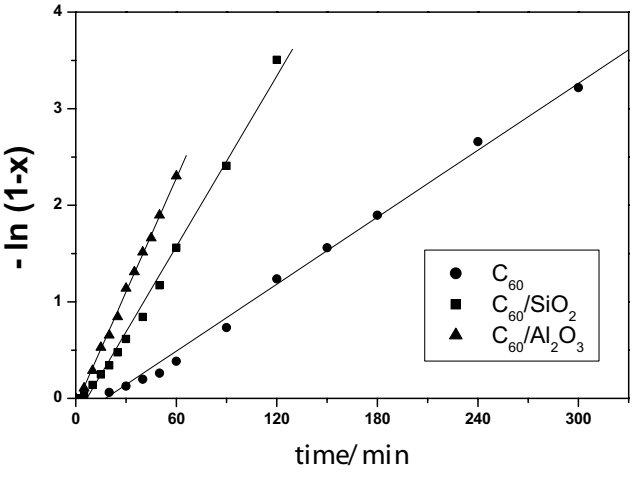


Figure 1. Graphical representation of the values of right-hand side of equation (2) with the time of photooxidation of 2-methyl-2-heptene over unsupported and supported C_{60}.

Table 2
Reaction-rate constant (k) for the photooxidation of 2-methyl-2-heptene, achieved using fullerene and supported fullerene as catalysts

Catalyst	k (min^{-1} $mol_{C_{60}}{}^{-1}$)
C_{60}	$2.4 \cdot 10^3$
C_{60}/SiO_2	$3.0 \cdot 10^5$
C_{60}/Al_2O_3	$4.0 \cdot 10_5$

lines of figure 1. These values are compiled in table 2 and show that two orders-of-magnitude increase in the photocatalytic activity of C_{60} is achieved by supporting it on SiO_2 and Al_2O_3 surfaces. This increase is higher when Al_2O_3 is used as a carrier.

The excellent effectiveness of both photocatalytic surfaces was also confirmed by the photooxidations of other alkenes, such as 2,3-dimethyl-2-butene and 2,4-dimethyl-2-pentene. By these studies, it was also proved that the photocatalytic activity of both catalysts remains intact after filtration and high vacuum distillation of the volatiles at room temperature.

We have also addressed the question why the deposition of fullerene on the surfaces of the carriers resulted in the high increase in the photooxidation activity observed. Table 3 shows that the carbon content of the prepared catalysts is very close to the nominal one (2% w/w), and the deposition of C_{60} on the carriers provoked only a slight decrease in their specific surface areas. The latter is a first, indeed weak, evidence that using the incipient wetness impregnation method and the 1,2-dichlorobenzene as solvent one can prepare samples of supported C_{60} on SiO_2 and Al_2O_3 surfaces, achieving a relatively high dispersion of the supported phase. This high dispersion is expected to result in a greater area of the "supported fullerene/reaction mixture interface" than that of the "unsupported fullerene/reaction mixture interface". The increase of the fullerene/reaction mixture interface area seems to be a key factor for the photocatalytic activity of fullerene in the studied reaction. To visualize better this point, we calculated the TONs achieved in two experiments performed under the same reaction conditions but using different concentrations, 10^{-4} and 5×10^{-3} M, of unsupported C_{60} as catalyst. This parameter is defined as the moles of alkene converted per mole of fullerene in the reactor. After irradiation of the reaction mixture for 150 min, the calculated TONs were 54 and 5, respectively. The increase of the C_{60} concentration in the second case could be responsible for an increase of C_{60} agglomeration and thus for a corresponding decrease of the fullerene/reaction mixture interface area, which, in turn, brings about the decrease of the catalytic activity.

Another, perhaps more significant reason for the above behavior may be the triplet–triplet (T-T) annihilation, the rate of which increases with C_{60} agglomeration [21–24]. Therefore, this process is expected to reduce the number of the triplet-excited C_{60} molecules available for generation of singlet oxygen in the experiment performed using a relatively high concentration of unsupported C_{60}. The decrease in the rate of the T-T annihilation due to surface dispersion of the sensitizer may also contribute to the relatively high efficiency of sensitization in the case of C_{60} supported on silica and alumina surfaces.

In order to investigate whether the support ensures high dispersion of the C_{60} inferred above, we used the diffuse reflectance spectroscopy (DRS). Figure 2 illustrates the DRS spectra of C_{60}/Al_2O_3 sample (c) and the corresponding spectra of the C_{60}/Al_2O_3 mechanical mixture after simple mixing (a) and after subsequent heating in air at 180 °C for 4 h (b). An inspection of this figure shows that the fullerene in the mechanical mixture exhibits a wide absorption band in the UV-Vis range. The intensity of this band is too low and a 15-times magnification was required to render it visible. However, some spreading of the C_{60} on the γ-Al_2O_3 surface is mainly manifested by the increase (decrease) of the intensity of this band in the low (high) wavelength side of the spectrum after heating of the mechanical mixture. Taking this change as an evidence for the spreading of the fullerene on the oxide surface and the spectrum (figure 2(c)) we can conclude that the dispersion achieved upon impregnation and subsequent drying is much higher in the case of C_{60}/Al_2O_3 sample. This conclusion is also supported by previously published results obtained using C_{60} suspended on various

Table 3
The fullerene content (C_{60}) of the prepared catalysts and their specific surface areas (SSA)

Catalyst	C_{60} (% w/w)	SSA ($m^2 g^{-1}$)
C_{60}/SiO_2	2.02	212
C_{60}/Al_2O_3	1.97	216

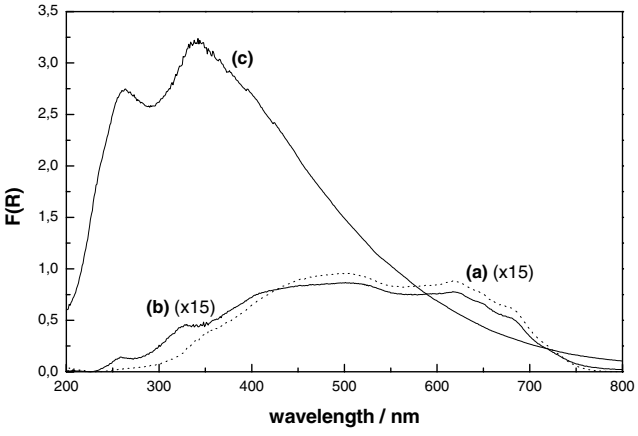


Figure 2. UV-Visible diffuse reflectance spectra of the C_{60}/Al_2O_3 mechanical mixture after mixing (a) and after heating at 180 °C for 4 h (b), as well as that of the C_{60}/Al_2O_3 sample (c). All spectra have been recorded using as reference γ-Al_2O_3.

solvents, which show that agglomeration of the fullerene molecules brings about a decrease in their absorbance coefficient in the UV-Visible region of the spectrum [25–28].

Finally, we compare the DRS spectra recorded for the two supported photocatalysts in order to justify the higher catalytic activity observed over the C_{60}/Al_2O_3 sample in comparison to that observed over the C_{60}/SiO_2 sample. As can be seen in figure 3, the DRS spectrum of the C_{60}/Al_2O_3 sample after drying is somewhat different from the corresponding spectrum of the C_{60}/SiO_2 sample. Although, both of them show enhanced absorption in the visible range of the spectrum, the relative absorption of the C_{60}/Al_2O_3 sample in the low-wavelength side of the spectrum is higher than that of the C_{60}/SiO_2 one. In line with the above and considering the absorption in the low-wavelength side of the spectrum by the supported fullerene as a measure of its dispersion on the surfaces of the carriers, one might easily explain the relatively higher catalytic activity exhibited by the C_{60}/Al_2O_3 sample. Taking into account that both supports have similar surface areas, the difference observed in the dispersion of C_{60} should be attributed in the different nature of the two oxides. For example, it is well known that alumina has a higher surface density of hydroxyl groups than silica [29]. These groups are expected to be the probable interaction sites with C_{60}. However, this point should be further investigated.

In order to investigate whether the structure of the fullerene does not change upon deposition on the carrier surfaces, extraction experiments were performed from the two supported samples using the 1,2-dichlorobenzene as solvent. The UV-Vis spectra of the extraction solutions were exactly the same with that of the impregnation one. This is good evidence that the structure of the fullerene is not destroyed during impregnation and the subsequent heating used for its deposition on the carrier surfaces. The extraction experiments also showed that a higher amount of fullerene is extracted from the C_{60}/SiO_2 sample. This indicates that the higher dispersion of C_{60} on the alumina surface concluded above is related with stronger or greater-in-extent interactions between the supported fullerene and the alumina surface than those exerted between the supported fullerene and the silica surface. The nature of these interactions is currently under investigation.

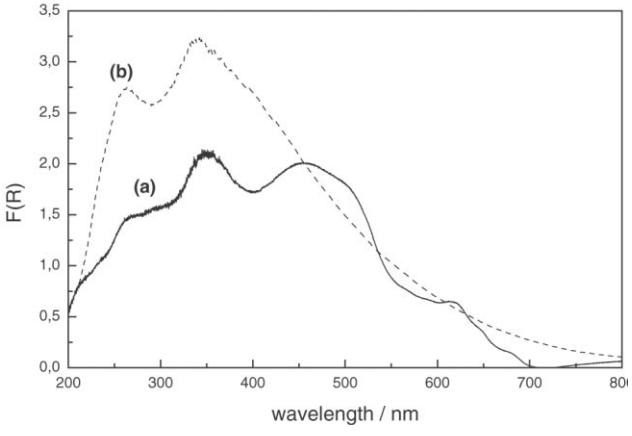


Figure 3. UV-Visible diffuse reflectance spectra of the C_{60}/SiO_2 (a) and the C_{60}/Al_2O_3 (b) samples after drying. These spectra have been recorded using the corresponding carries as reference samples.

4. Conclusions

The most important findings from the present study could be summarized as follows:

1. Very active photocatalysts for the liquid-phase oxidation of alkenes can be prepared by depositing fullerene C_{60} on silica and γ-alumina using the incipient wetness impregnation technique and the 1,2-dichlorobenzene as solvent. Alumina proved to be a better carrier than silica.
2. The use of supported fullerene on the silica and γ-alumina surfaces as photocatalysts does not change the reaction mechanism and its selectivity.
3. High dispersion of the supported fullerene is achieved on the surface of the carriers, which increase the fullerene light absorbance especially in the visible range.

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