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ZrO₂ BASED MATERIALS AS PHOTOCATALYSTS FOR 2-PROPANOL OXIDATION BY USING UV AND SOLAR LIGHT IRRADIATION AND TESTS FOR CO₂ REDUCTION

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Abstract

Bare ZrO₂, Ce doped ZrO₂ and Er doped ZrO₂ samples have been prepared by a hydrothermal process and have been used as photocatalysts for 2-propanol oxidation reaction in gas solid regime. Moreover, some preliminary tests have been carried out for CO₂ reduction. The samples were physico-chemically characterized and both bare and doped ZrO₂ based materials resulted active for oxidation and reduction reactions by using UV and solar irradiation. The reactivity results have been correlated with the compositional, structural and morphological features of the photocatalysts.

Keywords: photocatalysis, ZrO₂, Ce doped ZrO₂, Er doped ZrO₂, 2-propanol oxidation, CO₂ reduction

Introduction

Photocatalysis has been extensively used in the last thirty years in environmental chemistry to remove pollutants [1] or more recently for synthetic purposes [2,3]. TiO₂ has been one of the most investigated and active photocatalyst for environmental applications giving rise to mineralization of pollutants under UV irradiation, but it is poorly effective under solar irradiation. The search of new heterogeneous photocatalysts active under visible light has been the object of intense effort. Modifications of TiO₂ via doping with transition-metal ions, non-metal p-block elements or supported metal nanoparticles having plasmonic effects, constitute the second-generation photoactive materials, resulting in many cases more active than the pristine TiO₂. The continuous pursuit of active photocatalysts under visible light has addressed the research to a third generation of materials not based on TiO₂ [4]. ZrO₂ has been seldom applied in photocatalysis because of its wide band gap (ca. 5.0 eV), although some reports are available concerning photo-oxidation of chemicals [5], water photo-splitting [6] and CO₂ photoreduction [6-8]. The band energy levels of ZrO₂ are suitable for photocatalytic applications because the lowest potential of the conduction band (CB) is ca. -1.0 V (vs. NHE, pH 0), i.e. much more negative than that of TiO₂ anatase (-0.1 V), whereas the highest potential of the valence band (VB) is ca. +4.0 V, more positive than that of TiO₂ (+3.1 V). Introduction of new electronic states in the high band gap by doping with rare earth elements modifies the optical properties of the ZrO₂ giving rise to an active photocatalyst which can absorb also a fraction of the visible light. For instance, the presence of Ce(IV) ions in the bulk of ZrO₂ improved the photocatalytic activity of the oxide [9]. The activity of this third generation photoactive material, as Ce-ZrO₂, is based on the double excitation through localized intra-band-gap states [10,11]. The intra band gap Ce 4f empty states, which could act as a bridge between the VB and the CB of the ZrO₂, allows low-energy photons to excite electrons from the VB to the CB. A first type of photons provides the excitation of the electrons from VB to the Ce intra band gap states, a second one promotes the excited electrons into the CB, analogously to what occurs in the visible light active N-doped TiO₂ photocatalyst [12]. Also the role of Er in ZrO₂ has been studied. Ce and Er-doped ZrO₂ samples resulted photoactive in methylene blue removal in aqueous solution [13]. The TiO₂ doping 3d metal ions has been very much explored in the past to obtain visible light active photocatalysts, however the results obtained are very scarce because the metals act generally as recombination centers of the photogenerated carriers [14]. This phenomenon is due

to the partial population of the 3d states introduced at mid gap of TiO₂. The introduction of empty 4f states creates a different situation; indeed, the empty states as mid gap levels seem to be essential to obtain a photoactive material [15]. In the present paper ZrO₂ doped with Ce and Er with different loadings have been prepared giving rise to materials with different physico-chemical features. Their photocatalytic activity was tested in gas-solid regime for 2-propanol oxidation under UV and solar (artificial or natural) irradiation and for some preliminary tests for CO₂ reduction under simulated solar irradiation.

Experimental

2.1. Preparation and Characterization of the photocatalysts

The samples have been prepared by means of a hydrothermal process, starting from an aqueous solution containing the zirconium precursor (ZrOCl₂·8H₂O) in 1.0 M concentration and the rare earth (RE) precursor, (Ce(SO₄)₂ or Er(NO₃)₃·5H₂O). The pH of the solution was then adjusted to 11 by using a 4.0 M NaOH aqueous solution. The solution with the precipitates was then transferred into a 125 ml Teflon-lined stainless steel autoclave, 70% filled, which was heated at 175°C overnight in an oven. The precipitates were hence centrifuged and washed three times with deionized water, then dried at 60°C. For comparison pure ZrO₂ was prepared by the same procedure, without the presence of the RE. Finally, the prepared powders were calcined at 500°C for 2 h. For each dopant (Ce or Er) two samples with different RE content, namely 0.5% and 10 % molar percentage, were prepared. Samples will be labeled throughout the paper by using C for cerium and E for erbium, followed by a figure indicating the molar percentage of the dopant. For example: Z stands for pure zirconia, C05Z stands for the 0.5% mol Ce doped zirconia.

X-Ray Diffraction (XRD) patterns were recorded with a PANalytical PW3040/60 X'Pert PRO MPD using a copper K α radiation source (0.15418 nm) and a Bragg Brentano geometry. X'Pert High-Score software was used for data handling. Rietveld refinement was performed to determine the crystallite size and relative abundance of phases, using the MAUD 2.26 software and a NIST Si powder to determine the instrumental broadening. Raman measurements were performed on pure powdered samples and recorded by a micro Raman Mediatek i-Plus with a 785 nm laser diode. Surface area measurements were carried out on a Micromeritics ASAP 2020 using the BET model at five P/P⁰ points. The photoluminescence spectra were recorded by using a Jobin-Yvon spectrometer (Fluorolog 320) equipped with a 450 W Xenon lamp as the excitation source. Electron Paramagnetic Resonance (EPR) spectra were recorded at room temperature and at liquid nitrogen temperature (77K) on a X-band CW-EPR Bruker EMX spectrometer equipped with a cylindrical cavity operating at 100 kHz field modulation. The effect of light on EPR spectra was investigated by using a 1600 W Mercury/Xenon lamp (Oriel Instruments) and an IR water filter. A 400 nm cut off filter was used to eliminate part of the UV radiation, leaving a 5-8% of UVA component comparable to that present in the solar spectrum. Diffuse Reflectance Spectroscopy (DRS) data were recorded in the 200-800 nm range using a Varian Cary 5000 spectrometer, coupled with an integration sphere for diffuse reflectance studies, using a Carywin-UV/scan software. A sample of PTFE with 100% reflectance was used as the reference. The optical band gap energy has been calculated from the Tauc plot.

2.2. Photocatalytic experiments

The photoreactivity of the powders was studied for an oxidation model reaction in gas-solid regime. Moreover, some tests for CO₂ photo-reduction were carried out. The photocatalytic oxidation of 2-propanol was carried out in a cylindrical Pyrex batch photoreactor (V = 25 ml, ϕ = 45 mm, height = 15 mm) provided with a silicon/teflon septum. For the oxidation runs, the photocatalyst (0.06 g) was dispersed in the bottom of the photoreactor and O₂ was fluxed for ca. 0.5 h to ensure saturation. 1 μ l of liquid 2-propanol was introduced and vaporized in the batch reactor (C_o=0.54 mM). Irradiation started when the steady state conditions had been achieved, i.e. after that the system was maintained under dark conditions at room temperature to achieve the adsorption equilibrium of the substrate on the catalyst surface. All of the samples were studied by illuminating

the photoreactor, horizontally positioned, by an UV-LED IRIS40 at 365 nm (first set-up) or by a SOLARBOX apparatus (CO.FO.ME.GRA.), simulating the solar light, equipped with a 1500 W high pressure Xenon lamp (second set-up). The irradiance reaching the reactor, measured by a Delta Ohm DO 9721 radiometer equipped with a 315-400 nm sensor, resulted 45 W/m² in the first set-up and 10 and 1000 W/m² in the range 315-400 nm and 400-950 nm, respectively in the second set-up. Additional experiments were carried out under visible light irradiation by using a KNO₂ 1M solution as filter which cut off the UV radiation with wavelength lower than 400 nm. The runs were also carried out by using natural solar light as the irradiation source. The photon flux was measured every 5 minutes throughout the runs to estimate the energy impinging on the photoreactor. The reacting fluid was analyzed by withdrawing gaseous samples from the photoreactor by means of a gas-tight syringe. The concentrations of 2-propanol and of its degradation organic compounds were measured by using a GC-17A Shimadzu GC equipped with a HP-1 column kept at 40 °C and a FID.

The second set of photocatalytic tests, devoted to the photocatalytic reduction of CO₂ was carried out by using the same previously described batch photoreactor and the SOLARBOX apparatus. 0.06 g of photocatalyst were dispersed in the bottom of the photoreactor and N₂ was flushed for 2 h inside the system under irradiation in order to phodesorb possible impurities and/or carbon residues from the catalyst surface. Subsequently, the photoreactor was saturated with CO₂ containing the vapor pressure of water at 298 K. Aliquots of the gaseous reaction mixture were withdrawn at fixed irradiation times by using a gas-tight microsyringe. The evolution of the formed organic products was followed by a GC-2010 Shimadzu equipped with a Phenomenex Zebron Wax-plus column by using He as the carrier gas and a FID. CO was analysed by a HP 6890 GC equipped with a packed column GC 60/80 Carboxen-1000 and a TCD.

2. Results and discussion

2.1. Physico-Chemical characterization

XRD patterns of the prepared samples are reported in Figure S1. A mixture of both monoclinic (m-ZrO₂) and tetragonal (t-ZrO₂) polymorphs of zirconia was observed in all of them. In agreement with previous studies [13], the increasing of RE dopant amount led to the stabilization of the tetragonal polymorph.

A Rietveld refinement was performed on the XRD patterns and the results are reported in Table 1. The weight percentages of phases obtained are in agreement with the qualitative considerations. The cell parameters of the m-ZrO₂ phase are poorly influenced by the insertion of the RE dopant, while the lattice constants of t-ZrO₂ undergo a distortion which increases with the RE content. Moreover, the m-ZrO₂, both in the bare and doped oxides, presents some degree of anisotropy. Indeed, the peaks broadening is not constant; for this reason, we have used the Popa model [16] for the refinement of this phase and we have listed in Table 1 the maximum (D) and minimum (d) crystallite sizes obtained from the Rietveld refinement, along with the [1 1 0] and [-1 1 1] plans, respectively. The maximum crystallite sizes for the monoclinic phase are generally larger than those of the tetragonal one.

TABLE 1

Raman spectra obtained for all of the samples are reported in Figures S2 and S3. The characterization results are in good agreement with the crystalline ZrO₂ phases revealed by XRD. Moreover, in the sample C10Z the presence of CeO₂ was revealed by the band at 463 cm⁻¹, assigned to the characteristic F_{2g} mode of the symmetric stretching of oxygen atoms around cerium ions in the cubic fluorite structure of CeO₂ (see SI). Figure 1 reports the Kubelka-Munk transformation of the diffuse reflectance spectra normalized to 1 for all of the samples. An absorption shoulder centered at ca. 300 nm is clearly observed for the Ce doped samples in Figure 1 (A). The absorption in the UV-Vis range increases for all of the samples by adding the RE but the effect of Ce and Er ions is largely different as reported before [13]. The presence of the absorption band centered at 300 nm dominates the spectra of the C10Z sample overlapping the fundamental transition of zirconia. The shape of the spectrum is strongly similar to that of pure CeO₂ indicating that this absorption

could be related to the charge transfer transition from O 2p to Ce 4f. This finding could indicate the presence of CeO₂ on the surface of ZrO₂ for the CXZ samples in accord with Raman results. Probably the CeO₂ was very well dispersed on ZrO₂ and consequently its presence was not revealed by XRD analysis. The Erbium containing samples, on the other hand, show a smaller modification of the optical properties of the materials; indeed, all of the spectra are very similar each other, except for the small region enlarged in the inset of Figure 1 (B). Both the EZ samples present many absorption bands which are the fingerprint of the Er³⁺ ion, and the shoulder centered at 300 nm already present in the undoped materials. This band intensity increases with the Er content. The values of E_g were calculated by using the Tauc plot [17] and are reported in Table 1. The values were calculated by considering a direct transition for all of the samples except for C10Z, where an indirect transition was considered. For the C05Z sample two values are reported, one ascribable to the fundamental VB→CB transition of ZrO₂, and a second one due to the absorption band ascribable to the O 2p → Ce 4f charge transfer transition. The value of the band gap of ZrO₂ is not highly affected by the insertion of dopants, while the overall absorption is largely modified. Both RE10Z samples are indeed coloured.

FIGURE 1

The photoluminescence emission spectra at $\lambda_{exc}=365$ nm (i.e. 3.40 eV) are reported in Figure 2. Since the excitation energy is lower than E_g, the PL spectra can reflect the intra band gap defects present in the ZrO₂ samples. The pure ZrO₂ (Figure 2, (a) both (A) and (B)) presents a broad, asymmetric emission band centered at around 440 nm (i.e. 2.82 eV). This emission band was already reported in literature, and it is generally assigned to the radiative recombination of a photogenerated hole with an electron occupying an oxygen vacancy [18-20]. In the case of Ce doped samples (Figure 2, (A)), there is an evident suppression of the luminescence intensity, indicating a lower amount of intra band gap defects and thus a lower electron hole recombination rate. This effect is higher for the C05Z sample for which the luminescence intensity is nearly zero, while in the case of the C10Z sample the luminescence intensity is lower than that of pure zirconia but higher than that of the C05Z sample, probably because the C10Z sample absorbed more energy during the excitation due to its lower band gap (presence of well dispersed CeO₂). In the case of Er doped samples (Figure 2, (B)), the effect is different, depending on the RE concentration. The E05Z sample, indeed, shows an enhanced luminescence, indicating the formation of many oxygen vacancies as charge compensation for the introduction of aliovalent Er³⁺ ions. The E10Z sample, on the contrary, shows a total suppression of the luminescence intensity, except for the bands related to its f-f transitions, suggesting that in this case the main recombination centers are actually the Er ions and not the formed oxygen vacancies.

FIGURE 2

EPR is a suitable technique to monitor the photo-induced charge separation process and, thus, to assess the photoactivity of a material under irradiation. Indeed, the direct charge separation is obtained by irradiating in situ the solid at the temperature of liquid nitrogen to avoid the rapid recombination of the carriers. If the photogenerated charges are stabilized by the solid (at different sites of the oxide, usually a cation for the electron and an oxide anion for the hole) paramagnetic centers can be formed (i.e. the O⁻ ion) and they can be monitored by the electron paramagnetic resonance. The effect of UV-Vis light on hydrothermally synthesized ZrO₂ was already reported by some of us [13]. The as prepared sample does not show paramagnetic centers and its spectrum is a barely flat line. Upon irradiation a new signal appeared ascribable to the photogenerated holes localized at an anion center. Figure S4 reports the EPR spectra recorded at liquid nitrogen temperature for the CZ (Figure S4 (A)) and EZ (Figure S4 (B)) samples. For all of the samples, both the spectra before ((a), (c)) and after ((b), (d)) irradiation for 15 minutes, are reported. The spectrum of the as prepared C10Z sample shows some intrinsic defectivity. It presents two signals, one centred at g=1.978 and assignable to Zr³⁺ species [21], and another one with g_{||}=1.96 and g_⊥=1.94, already reported in literature, and whose assignment is still

under debate [22-24]. Under irradiation a new signal, ascribable to O^- species, appears in both C05Z and C10Z samples. The effect of irradiation is much more evident in the case of the C05Z sample, whilst for C10Z the intensity of the new signal is much lower. This can be due to spin-orbit coupling effects that affect the localization of the photogenerated charges. The spectrum of the as prepared E05Z sample also shows the presence of a well-defined axial signal at $g_{\parallel}=1.978$ and $g_{\perp}=1.955$, which is assigned to Zr^{3+} ions, probably due to the aliovalency of Er^{3+} ions and the consequent formation of oxygen vacancies. Upon irradiation both the spectra of the E05Z and E10Z samples show the formation of the signal related to the localized hole. Also in this case the intensity of the spectrum of E05Z is higher than that of E10Z.

2.2.1. 2-Propanol oxidation

Preliminary experiments indicated that the contemporary presence of O_2 , catalyst and light was needed for the occurrence of 2-propanol degradation. After the equilibration time under dark conditions, the initial substrate concentration resulted in any case lower than the nominal one because 2-propanol was partially adsorbed on the samples surface. The extent of 2-propanol adsorption was ca. 50 % for the Ce doped and E05Z samples and 80 % for the E10Z powder. 2-Propanol concentration generally decreased with irradiation time and contemporaneously propanone concentration increased. For almost all of the runs an initial increase of 2-propanol concentration with the irradiation time, due to a slight photo/thermal desorption of the substrate, was observed. Due to the large amount of 2-propanol adsorbed on the samples, it was not possible to compare the photocatalytic activity of the various solids by following the disappearance of the substrate and to close the carbon mass balance. Hence, in order to compare the activity of the various photocatalyst it appears appropriate to follow the kinetic of propanone appearance. Figure 3 reports the evolution of propanone versus the irradiation time for all of the photocatalytic experiments carried out by using the three different irradiation sources. Propanone formation was always linear with the irradiation time and the calculated data of the initial reaction rates are reported in Table 2.

FIGURE 3
TABLE 2

By considering the experiments carried out by using the LED light source, the results indicate that the Ce doped samples showed the highest photocatalytic activity, improving the pristine ZrO_2 performance. The activity increased with the Ce content, resulting C10Z the most active material. On the contrary, the Er doping appeared to be detrimental for the photocatalytic 2-propanol oxidation with respect to the activity observed for the bare ZrO_2 . Moreover, it can be observed that the reactivity decreased by increasing the Er content. The experiments carried out both under artificial and natural solar irradiation confirm this behaviour, although the photocatalytic activity appeared much lower indicating that the activity of the materials can be attributed mainly to the UV light contribution in the solar source. In order to better understand this finding some runs were carried out by irradiating the system in the presence of a cut-off filter ($\lambda < 400$ nm). These runs confirmed our hypothesis as a very low activity was observed. Notably the initial reaction rates for the propanone formation, expressed as function of the cumulative energy entering the photoreactor, were similar for the artificial and natural solar irradiation by using the same photocatalyst, as reported in Table 2. Slight differences in the figures could be due to slight differences in the energy distribution between the two irradiation sources. The photo-activity of bare ZrO_2 under UV irradiation can be explained by taking into account the photoluminescence and EPR studies indicating that this material was able to photoproduce electron-hole pairs under UV light irradiation (in the PL $\lambda_{exc}=365$ nm), although its band gap is 5.2 eV. The presence of Ce induced a double excitation through localized intra-band-gap states as already reported [10,11] and consequently the photoactivity of the Ce doped material increased. The most active sample resulted C10Z in which the presence of CeO_2 was confirmed by the Raman spectra. In this case, the presence also of CeO_2 with a band gap of 3.0 eV was beneficial for the photo-activity of the sample. As far as the reactivity of Erbium doped ZrO_2 samples

is concerned, the double excitation through localized intra-band-gap states should be also considered as in the case of Ce doped material, but a decrease of the reactivity with respect to that observed for pristine ZrO₂ was found. This finding can be probably due to the fact that Erbium acted basically as a recombination centre of the photogenerated carriers.

2.2.2. Simulated solar irradiation: tests for CO₂ reduction

Blank tests carried out in the same experimental conditions ensured that no organic compounds were produced in the absence of catalyst as well as under dark or in the absence of CO₂.

All of the samples showed activity for CO₂ photo-reduction giving rise to small organic molecules and CO. This preliminary investigation was aimed only to demonstrate the versatility of these catalysts towards the CO₂ reduction reaction. During the first 6 h of irradiations ethanal and traces of methane, methanol, methanal, propanal and propanone were obtained. In all cases, the amount of the organic species increased by increasing the irradiation time and ethanal was always the product obtained in higher concentration. In particular, the maximum amount of ethanal revealed was ca. 15 μmol·g⁻¹ and 25 μmol·g⁻¹ after 6 h and 24 h of irradiation, respectively. Some catalysts gave rise also to formation of CO being the maximum amount formed ca. 5-6 μmol·g⁻¹, depending on the catalyst used. These amounts were reached after 6 h and remained constant for higher irradiation times. It was out of the aim of the present paper to compare the various photocatalysts at this stage of investigation. The amount of products formed, however, are in the same magnitude order as those reported in the literature for other powders.

The same reaction has been carried out by using the same set-up in the presence of TiO₂ photocatalysts obtained from TiCl₄ as the precursor [25]. In that case, depending on the type of catalyst, a different selectivity was observed but the main reaction product observed was also ethanal in a maximum amount of ca. 1 μmol·g⁻¹ after 5 h of irradiation. Also, GaP/TiO₂ materials were used before in the same system [26]. In that case the main product obtained by the CO₂ reduction was methane in an amount of ca. 12 μmol·g⁻¹ after 6 h of irradiation. However, a more thorough investigation is necessary in order to understand the different selectivity of various photocatalysts reported in the literature. Work is in progress by using the ZrO₂ based materials described in this paper.

Conclusions

The preparation of ZrO₂ by a solvothermal method and the introduction of new electronic states in this high band gap semiconductor by doping with Ce and Er, leads to new photocatalysts able to absorb portions of UV (λ=365 nm) and solar light. Pristine ZrO₂ as well as Ce and Er-doped ZrO₂ resulted photoactive in gas-solid regime for 2-propanol photooxidation to propanone and in CO₂ reduction to form mainly ethanal.

This uncommon behaviour for an insulator like ZrO₂ (with a band gap of more than 5 eV) is explained by the formation of intra band gap states. In the doped materials, these are formed by the f orbitals of the lanthanides. The intra band states are responsible for the “double jump” absorption leading to excitation of the electrons from the valence band to the conduction band.

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Table 1. Cell parameters, weight percentage and crystallite size obtained from Rietveld refinement: (Wt) weight percentage of a given phase; (*a*), (*b*) and (*c*) lattice parameters; (β) angle between *a* and *c* axes for the monoclinic cell; (*D*) and (*d*) maximum and minimum crystallite sizes for the anisotropic m-ZrO₂; (*d'*) crystallite size for t-ZrO₂; (E_{gap}) estimated band gap for all of the samples prepared.

Sample	Phase	Wt [%]	<i>a</i> [Å]	<i>b</i> [Å]	<i>c</i> [Å]	β [°]	<i>d</i> , <i>d'</i> [nm]	<i>D</i> [nm]	E_{gap} [eV]
Z	m-ZrO ₂	66	5.18	5.22	5.34	99.59	9	43	5.2
	t-ZrO ₂	34	3.58		5.23		7		
C05Z	m-ZrO ₂	61	5.19	5.22	5.35	99.71	13	40	5.1/4.0
	t-ZrO ₂	39	3.62		5.16		10		
C10Z	m-ZrO ₂	24	5.16	5.20	5.32	99.35	17	20	3.0
	t-ZrO ₂	76	3.62		5.17		10		
E05Z	m-ZrO ₂	76	5.17	5.21	5.33	99.51	15	31	5.2
	t-ZrO ₂	24	3.61		5.16		11		
E10Z	m-ZrO ₂	28	5.18	5.22	5.35	99.58	12	63	5.1
	t-ZrO ₂	72	3.64		5.16		12		

Table 2. Initial reaction rates (r_0) for the photocatalytic propanone formation by using the artificial irradiation (LED), the SOLARBOX apparatus or the natural solar light as irradiation sources by considering time or the energy entering the photoreactor.

Sample	SSA (m ² ·g ⁻¹)	r_0 (mol·L ⁻¹ ·min ⁻¹) 10 ⁸		r_0 (mol·L ⁻¹ ·J ⁻¹) 10 ⁸	
		LED	SOLAR BOX	SOLAR LIGHT	SOLAR BOX
Z	44	24	4.0	3.7	5.0
C05Z	66	29	5.4	5.2	7.1
C10Z	80	44	8.2	7.3	10
E05Z	75	13	4.2	2.4	5.1
E10Z	96	9.4	1.4	0.8	1.7

Caption for figures

Figure 1. Absorbance spectra of the samples obtained by applying the Kubelka-Munk function, $F(R_\infty)$, to the diffuse reflectance spectra. (A): Z (a), C05Z (b), C10Z (c) and (B): Z (a), E05Z (b), and E10Z (c) The inset is a magnification of the squared region.

Figure 2. Photoluminescence spectra of (A): Z (a); C05Z (b) and C10Z (c) and (B): Z (a); E05Z (b) and E10Z (c). Beware of the different intensity scaling of the spectra.

Figure 3. Propanone evolution versus the irradiation time for all the catalytic tests carried out with the three different irradiation source (LED, SOLARBOX, SUNLIGHT).

*Superscript numbers indicate the cumulative energy [J].