



Photocatalytic partial oxidation of limonene to 1,2 limonene oxide†

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The silylation of crystalline TiO₂ P25, commonly used for photocatalytic degradation of pollutants, results in an exceptionally selective catalyst for the aerobic limonene epoxidation to 1,2-limonene oxide under solar light irradiation. The hypothesized mechanism involves the singlet oxygen generated through energy transfer from the excited TiO₂ to adsorbed O₂ molecules. The reaction product is the valued precursor of bio-based poly(limonene carbonate), a thermoplastic polymer of superior thermal and optical properties whose industrial production is in need of an efficient green synthesis of limonene oxide.

D-Limonene is a cyclic terpene with a strong smell of oranges, widely used in cosmetic products, perfumery, and as a solvent.¹ Its natural abundance makes it a promising substrate for various chemical processes. Currently obtained on small scale in industry by reacting limonene with perchloric acid (Prileschajew reaction), 1,2-limonene oxide (LO) is a valued bio-based building block whose copolymerization with carbon dioxide catalysed by a β-diimine zinc acetate catalyst affords poly(limonene carbonate),² a biodegradable polymer of exceptional thermal resistance, hardness and transparency.³ Epoxidation of D-limonene generally affords different isomers (*cis*- and *trans*-) depending on the double bonds (exo- and/or endo-cyclic) involved. Therefore, selective synthetic routes towards internal *cis*- and *trans*-epoxides (Fig. 1) are highly desired, with the alternating polycarbonate copolymer produced from a *cis/trans* mixture of limonene epoxide (1,2-limonene oxide, Fig. 1) being highly regio- and stereoregular.²

Besides homogeneously catalyzed processes⁴ which require catalyst separation from the reaction mixture and product purification (discouraging industrial application), several new heterogeneously catalyzed limonene epoxidation routes have

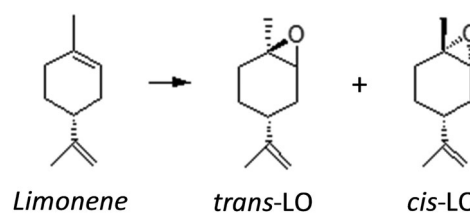


Fig. 1 Chemical structures of limonene, *trans*- and *cis*-limonene oxide (LO).

been developed in the last decade. Suffice it to mention here the epoxidation of limonene dissolved in ethyl acetate over Al₂O₃ using hydrogen peroxide as a green oxidant at 80 °C affording a mixture of internal and external epoxides in >99% yield;⁵ and that in acetonitrile over Ti-SBA-16 with anhydrous *tert*-butyl hydroperoxide affording at 75 °C optimal 80% limonene conversion with 1,2-limonene oxide selectivity of 79%.⁶ Photocatalytic studies concerning limonene oxidation mostly deal with its photochemical mineralization to CO₂, as limonene is a frequent indoor allergenic pollutant.⁷ Hereby we report that silylation of commercial TiO₂ photocatalyst P25 affords an excellent catalyst (Sil-P25) for D-limonene epoxidation under solar light irradiation with O₂ as the unique primary oxidant. In detail, highly hydrophobic Sil-P25 was obtained by treating P25 with hexadecyltrimethoxysilane according to the experimental procedure described in the ESI.† A solution of D-limonene (1 mM) in acetonitrile (5 mL) was flushed with 1 bar O₂ several times at room temperature. The reaction vessel was sealed and inserted in a solar light simulator (Solar Box, CO.FO.ME.GRA., Milan) equipped with a Xe lamp (1500 W, no UV filter, see Fig. S1 in the ESI†), under vigorous magnetic stirring. Results in Table 1 show evidence that after 2 h, 54% of substrate is converted with about 90% selectivity to LO (mixture of *cis*- and *trans*-LO, molar ratio ca. 2.5/1). Prolonging the reaction time decreases the reaction selectivity, as it is commonly observed for other synthetic photocatalytic reactions.⁸ No product formation was observed in the absence of oxygen. Notably, while conventional anchoring groups (carboxyl, phosphonate or amido linkages) undergo certain degree

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Table 1 Limonene conversion and selectivity to 1,2-limonene oxide (mixture of *cis* and *trans*, molar ratio *ca.* 2.5/1) in acetonitrile under O₂ atmosphere and simulated solar light irradiation over different TiO₂-based photocatalysts^a

Catalyst	Entry	Reaction time (h)	D-Limonene conversion (%)	LO selectivity (%)
Sil-P25	1	1	10.0	48.2
	2	2	54.0	87.7
	3	3	79.3	54.0
P25	4	1	75.0	29.5
	5	2	83.8	30.0
	6	3	94.3	11.7
F-P25	7	1	81.7	20.3
	8	2	91.7	3.2
	9	3	98.0	0
HP05	10	1	77.3	21.5
	11	2	98.8	5.5
	12	3	100	2.1
HP05C	13	1	78.9	31.4
	14	2	96.0	35.6
	15	3	100	19.2
Sil-HP05	16	1	15.5	28.7
	17	3	46.1	11.6
	18	6	60.6	10.7

^a Figures are the average of results obtained in three independent runs carried out under the same experimental conditions. P25 = commercial TiO₂ (Evonik); Sil-P25 = silylated P25; F-P25 = fluorinated P25; HP05 = home-prepared TiO₂ sample; HP05C = HP05 calcined at 400 °C for 4 h; Sil-HP05 = silylated HP05.

of dissociation or dechelation, the silyl group is reported as the most stable surface modification moiety.⁹ As far as the alkyl chain is concerned, only slow oxygenation of the secondary carbons is reported during photocatalytic degradation of linear alkanes, without chain cleavage reactions.¹⁰ Accordingly, the stability of Sil-P25 was confirmed by repeating the epoxidation reaction three times with the same powder recovered after each run. Conversion was virtually the same in all of the three runs, while selectivity slightly increased, possibly due to desorption of the product formed in the previous run.

Bare P25 TiO₂ (Evonik, 20% rutile and 80% anatase) is reported to be a good photocatalyst for limonene degradation under UV light in gas phase, though with significant formation of submicron particulate matter (PM10).¹¹ In the present experimental conditions we observed good photocatalytic activity also under solar light irradiation, with a substrate conversion of more than 90% after 3 h (entry 6, Table 1). However, lower selectivity towards LO was observed with respect to the silylated powder. In fact, only 30% selectivity at *ca.* 84% conversion was obtained after 2 h solar irradiation. Hence, P25 was fluorinated, and the resulting catalyst F-P25 used for the same aerobic photooxidation (entries 7–9). In this case the activity of F-P25 was higher than that of bare P25, while the selectivity towards LO at similar conversion values was lower (see entries 5 and 7), and then dramatically decreased until complete consumption of LO.

In various photocatalytic syntheses mediated by crystalline TiO₂, reducing the crystallinity of the photocatalyst enhances

the selectivity towards the desired products by reducing the activity.¹² In fact, generally, the highly ordered crystal lattice of titanium dioxide favours the mineralization path with respect to the adsorption/desorption steps. This produces detrimental effects on the selectivity as the target products are mineralized before being desorbed.¹³ For this reason we also investigated a home prepared powdered TiO₂ photocatalyst (HP05) consisting mainly of amorphous TiO₂ (*ca.* 92%) along with crystals of anatase and rutile, selective in the aerobic oxidation of *trans*-ferulic acid.¹⁴ Although the activity of HP05 was comparable with that of P25, lower LO selectivity was achieved (entries 10–12). Therefore, higher crystallinity seems to be beneficial in terms of selectivity for the present terpene oxidation. To confirm this hypothesis HP05 sample was calcined at 400 °C for 4 h and used in the same reaction. As expected, calcination allowed to achieve higher LO selectivity, while similar conversion could be obtained. This result may be tentatively attributed to the different morphological features of the two TiO₂ samples (reported in the ESI,† Fig. S2 and Table S1) and to the specific interaction of limonene with the photocatalyst surface. Further investigations are ongoing to unravel the interplay between these factors and the selectivity and conversion values hereby obtained. Silylation of HP05 (Sil-HP05) afforded results qualitatively analogous to the case of Sil-P25, leading to lower activity and higher selectivity towards LO with respect to the unmodified HP05 sample.

Fig. 2 displays the trend of selectivity towards LO during irradiation time for bare and modified P25-based samples.

All of the P25-based catalysts show a similar selectivity pattern, reaching a maximum and then decreasing for longer irradiation times. Bare P25 displayed intermediate selectivity values, in between those of Sil-P25 and F-P25 which showed the highest and the lowest selectivity, respectively. The photocatalytic oxidation of limonene over multiwalled carbon nanotube/P25 TiO₂ composite under visible-light irradiation affords various oxidation products among which LO was detected as a minor product.¹⁵ The tentative mechanism involves oxidation of limonene by the photogenerated holes (directly or mediated by surface trapping) or by attack of superoxide anions (O₂^{•-}) and OH radicals (•OH) generated by interfacial charge transfer. Although •OH production is much

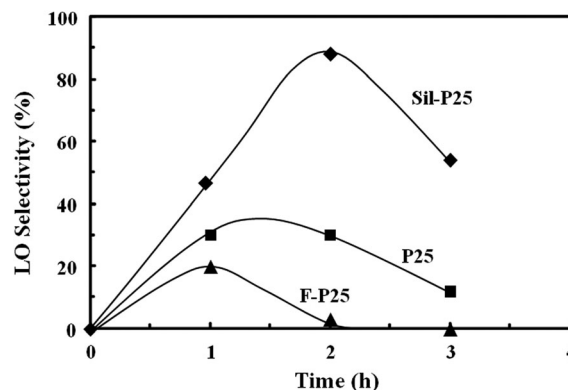


Fig. 2 Selectivity values towards LO during irradiation time in the presence of silylated P25 (diamonds), P25 (squares), and fluorinated P25 (triangles) photocatalysts.

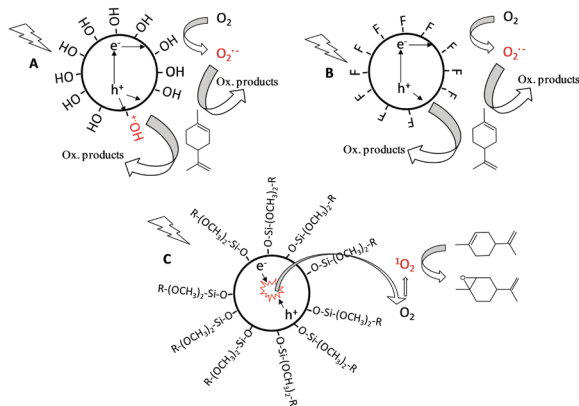


Fig. 3 Oxidation of limonene in the presence of bare P25 (Scheme A), fluorinated P25 (Scheme B) and silylated P25 ($R = C_{16}H_{33}$, Scheme C). Although anchoring may occur through all of the three methoxy groups of the silane, only one oxygen bridge per silane molecule has been depicted for the sake of clarity.

lower in acetonitrile than in aqueous suspension, this mechanism may be invoked in the present conditions for P25 suspensions (Scheme A, Fig. 3). The behaviour of the F-P25 sample, fast degradation and low LO selectivity, confirms that the above mentioned mechanism produces LO only as a minor product. In fact, while $\equiv Ti-OH$ sites on the TiO_2 surface act as hole traps leading to the formation of $\equiv Ti-O^{\bullet}$ and H^+ species, the $\equiv Ti-F$ surface species cannot be oxidized because of the overly high potential (3.6 V) of the F^{\bullet}/F^- couple.¹⁶ For this reason the enhanced direct hole transfer efficiency to limonene over fluorinated P25 gives place to its fast oxidation and lower selectivity towards LO (Scheme B, Fig. 3).

The superior selectivity towards LO of the Sil-P25 sample compared to the other materials may be due to the hydrophobic nature of the surface decorated with long (C16) alkyl chains. This enhances the affinity of hydrophobic D -limonene for the organically-modified TiO_2 surface, while favouring desorption of the more polar oxygenated products thus hindering their further oxidation as reported for example in the case of photocatalytic conversion of cyclohexane to cyclohexanone over similar silylated TiO_2 .¹⁷ On the other hand, the surface silylation of P25 suppresses interfacial charge transfer due to the alkyl chains blocking the active sites so that recombination is the most probable fate of the photogenerated charges (Scheme C, Fig. 3), with the energy thereby made available being transferred to molecules close to the photocatalyst particles to initiate chemical reactions. Both charge and energy transfer may afford the same products, and consecutive reactions or adsorptive phenomena make it difficult to differentiate them in heterogeneous photocatalysis. Notably, charge transfer inhibition by surface modification is an elegant way to highlight the role of energy transfer. In fact, although the energy transfer mechanism may occur in irradiated TiO_2 suspensions, it prevails in the silylated samples at the expense of the interfacial electron transfer. Rare examples are reported in literature such as the TiO_2 induced isomerisation of caffeic acid¹⁸ or the degradation of cyanuric acid by singlet oxygen (1O_2).¹⁹ The present reaction testifies that

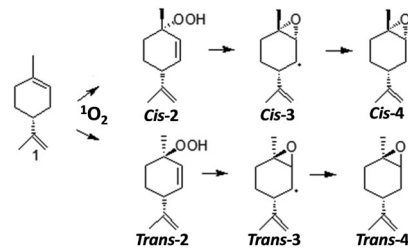


Fig. 4 Reaction mechanism of limonene with singlet oxygen to *cis*- and *trans*-LO.

energy transfer may be exploited also for synthetic applications. Indeed, in this case the singlet oxygen gives place to the Schenk reaction²⁰ with limonene according to the mechanism displayed in Fig. 4. 1O_2 adds to the endocyclic electron-rich double bond affording a hydroperoxide which rearranges to radical epoxide. The latter abstracts a hydrogen atom, possibly from another limonene molecule, eventually affording 1,2-limonene oxide (4).

According to this mechanism, both *cis*- and *trans*-LO may be formed. In the present experimental conditions, the *cis* form was in each case favoured as its concentration is *ca.* 2.5 times higher than the *trans* isomer. To confirm the role of singlet oxygen in the LO formation, a qualitative test was performed without TiO_2 but in the presence of the xanthene dye Rose Bengal (RB) which is a well known precursor of singlet oxygen under visible light irradiation.²¹ To our delight, formation of LO was clearly observed though with a lower selectivity (*ca.* 6%) compared to the TiO_2 -mediated oxidation. Indeed, highly unstable RB undergoes strong photobleaching,²² with formation of radicals and peroxides, and the characteristic pink color of the solution vanishing after 1 hour irradiation.

In conclusion, the high-yield and selectivity obtained in the photocatalytic aerobic oxidation of D -limonene to 1,2-limonene epoxide under the solvent-free and remarkable mild conditions reported in this work may open the route to the solar synthesis of limonene epoxide on large scale. To this aim, the yield may be further improved by integrating the reacting system with a separation unit capable of continuously extracting the desired epoxide from the photocatalytic suspension thus avoiding its overoxidation. This approach has been successfully used and optimized for the green synthesis of vanillin carried out in a photocatalytic membrane reactor.²³ The robustness, low cost and highly porous nature of the Sil-P25 sol-gel catalyst, indeed, make it ideal for utilization in a transparent photochemical flow reactor such as one of those lately developed for the photocatalytic synthesis of fine chemicals and active pharmaceutical ingredients.²⁴

This article is dedicated to Professor Kevin Booker-Milburn, University of Bristol, for all he has done for the progress of synthetic photocatalysis introducing the photochemical flow reactor.

Conflicts of interest

There are no conflicts to declare.

References

- 1 R. Ciriminna, M. Lomelli, P. Demma Carà, J. Lopez-Sanchez and M. Pagliaro, *Chem. Commun.*, 2014, **50**, 15288–15296.
- 2 C. M. Byrne, S. D. Allen, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2004, **126**, 11404–11405.
- 3 O. Hauenstein, M. Reiter, S. Agarwal, B. Rieger and A. Greiner, *Green Chem.*, 2016, **18**, 760–770.
- 4 T. Michel, M. Cokoja, V. Sieber and F. E. Kühn, *J. Mol. Catal. A: Chem.*, 2012, **358**, 159–165.
- 5 A. J. Bonon, Y. N. Kozlov, J. O. Bahú, R. Maciel Filho, D. Mandelli and G. B. Shul'pin, *J. Catal.*, 2014, **319**, 71–86.
- 6 L. Charbonneau and S. Kaliaguine, *Appl. Catal., A*, 2017, **533**, 1–8.
- 7 B. Mull, L. Möhlmann and O. Wilke, *Environ.*, 2017, **4**, 9.
- 8 V. Augugliaro, H. Kisch, V. Loddo, M. J. Lopez-Munoz, C. Marquez-Alvarez, G. Palmisano, L. Palmisano, F. Parrino and S. Yurdakal, *Appl. Catal., A*, 2008, **349**, 189–197.
- 9 A. K. M. Fung, B. K. W. Chiu and M. H. W. Lam, *Water Res.*, 2003, **37**, 1939–1947.
- 10 P. Pichat, *Catal. Today*, 1994, **19**, 313–333.
- 11 H. Ourrad, F. Thevenet, V. Gaudion and V. Riffault, *Appl. Catal., B*, 2015, **168–169**, 183–194.
- 12 M. Bellardita, V. Loddo, A. Mele, W. Panzeri, F. Parrino, I. Pibiri and L. Palmisano, *RSC Adv.*, 2014, **4**, 40859–40864.
- 13 M. A. Lazar and W. A. Daoud, *RSC Adv.*, 2012, **2**, 447–452.
- 14 F. Parrino, V. Augugliaro, G. Camera-Roda, V. Loddo, M. J. López-Muñoz, C. Márquez-Álvarez, G. Palmisano, L. Palmisano and M. A. Puma, *J. Catal.*, 2012, **295**, 254–260.
- 15 W.-K. Jo and H.-J. Kang, *J. Hazard. Mater.*, 2015, **283**, 680–688.
- 16 M. Mrowetz and E. Selli, *Phys. Chem. Chem. Phys.*, 2005, **7**, 1100–1102.
- 17 A. R. Almeida, J. T. Carneiro, J. A. Moulijn and G. Mul, *J. Catal.*, 2010, **273**, 116–124.
- 18 F. Parrino, A. Di Paola, V. Loddo, I. Pibiri, M. Bellardita and L. Palmisano, *Appl. Catal., B*, 2016, **182**, 347–355.
- 19 A. Janczyk, E. Krakowska, G. Stochel and W. Macyk, *J. Am. Chem. Soc.*, 2006, **128**, 15574–15575.
- 20 A. A. Frimer, *Chem. Rev.*, 1979, **79**, 359–387.
- 21 M. C. DeRosa and R. J. Crutchley, *Coord. Chem. Rev.*, 2002, **233–234**, 351–371.
- 22 M. Roncel, J. A. Navarro and M. A. de la Rosa, *J. Photochem. Photobiol., A*, 1988, **45**, 341–353.
- 23 G. Camera-Roda, V. Loddo, L. Palmisano, F. Parrino and F. Santarelli, *Chem. Eng. J.*, 2017, **310**, 352–359.
- 24 R. Ciriminna, R. Delisi, Y.-J. Xu and M. Pagliaro, *Org. Process Res. Dev.*, 2016, **20**, 403–408.