

Supporting Information

Photocatalytic partial oxidation of limonene to 1,2 limonene epoxide

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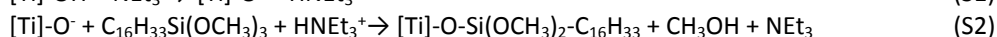
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Experimental

The TiO₂ samples used were the commercial P25 (Evonik, specific surface area ca. 50 m² g⁻¹), comprised of anatase (80%) and rutile (20%), and the home prepared HP05 sample, mainly amorphous (92%) with crystals of anatase (75%) and rutile (25%), specific surface area 235 m² g⁻¹. HP05 sample was obtained by slowly adding 5 mL of TiCl₄ (Sigma-Aldrich, ≥ 99%) drop wise into 50 mL of water in a beaker under magnetic stirring. After that, the beaker was closed and mixing was prolonged for 12 h at room temperature, eventually obtaining a clear solution. This solution was boiled at 373 K for 0.5 h obtaining a white suspension that was then dried at 323 K in order to obtain the final solid. The powder was finally washed with distilled water and centrifuged several times until the chloride ion concentration in the washing water reached a negligible value.

Silylation of TiO₂ P25 and HP05 was performed as follows: In a round bottom flask were mixed 1g of TiO₂, 50 ml of n-hexane (Sigma-Aldrich, p.a.), 2 ml of triethylamine (Sigma-Aldrich, ≥ 99%) and 7 g of hexadecyltrimethoxysilane C₁₆H₃₃Si(OCH₃)₃ (Sigma-Aldrich, ≥ 85%). The suspension was boiled at 90° C for 24 h. The solid phase was separated from the liquid by centrifugation and washed three times with n-hexane. The powder was dried at room temperature in vacuum and finally ground.

The silylation process may be described according to Eqs. S1 and S2.



The base triethylamine reacts with the acidic groups on TiO₂ giving the strong base [Ti]-O⁻ which in turn attacks the silicon atom affording an oxygen bridge between Ti and Si. Concomitant elimination of CH₃OH reforms triethylamine. Similarly, the remaining methoxy groups (OCH₃) can be also replaced by other TiO groups. Notably, the silylation process may be safely assumed as quantitative in the present experimental conditions, by considering the long reaction time, high temperature and that both triethylamine (14.35 mmol) and hexadecyltrimethoxysilane (20.2 mmol) were used in large excess with respect to the OH groups to be replaced (0.46 and 6.32 mmol g⁻¹ for P25 and HP05 samples, respectively).^{S1}

Fluorinated P25 was prepared by the impregnation method. 1g of P25 was impregnated in 50 ml of 4% NaF solution at pH 3.2 (pH adjusted by HNO₃) for 2 days at room temperature. The powder separated by centrifugation was washed two times with water at pH 3.2, dried in vacuum at 80°C for 2h and finally ground.

Specific surface area, porosity, and particle size of the home prepared HP05 and HP05C samples were measured by a Micromeritics Accelerated Surface Area and porosity (ASAP 2020) apparatus with N₂ as the adsorbate. X-ray diffraction (XRD) patterns were recorded at room temperature by an Ital Structures APD 2000 powder diffractometer, using the Cu Kα radiation and a 2θ scan rate of 2° min⁻¹.

Samples of the runs have been filtered by means of syringe filters (Whatman 0.2 μm) and analyzed by means of an HP 5890 GC-MS equipped with the mass selective detector HP 5973. An HP5-MS, 5% diphenyl-95% dimethylpolysiloxane capillary column (30 m, 0.25 mm, 0.25 μm film thickness) was used as stationary phase. Chromatographic conditions: 1 μL split 1:10 injection by autosampler, carrier gas He at 10^{-3} L min^{-1} , injector temperature 250 $^{\circ}\text{C}$. Oven temperature program: 1 min of 40 $^{\circ}\text{C}$ isotherm followed by a linear temperature increase of 5 $^{\circ}\text{C min}^{-1}$ up to 200 $^{\circ}\text{C}$ held for 5 min, followed by an increase of 15 $^{\circ}\text{C min}^{-1}$ up to 280 $^{\circ}\text{C}$. MS scan conditions: source temperature 230 $^{\circ}\text{C}$, interface temperature 280 $^{\circ}\text{C}$, Energy 70 eV, mass scan range 39–350 amu. Linear retention indices were calculated with references to *n*-alkanes (C6–C20), obtained from FLUKA, and run under the chromatographic condition described above. Identification of the compounds was performed using a commercial library (NIST) and a FFC (flavour and fragrance components) bank provided with linear retention indices determined on the same column, to be used interactively with MS data for compound identification. Standard mixtures of selected identified standard compounds were also injected to obtain quantitative responses.

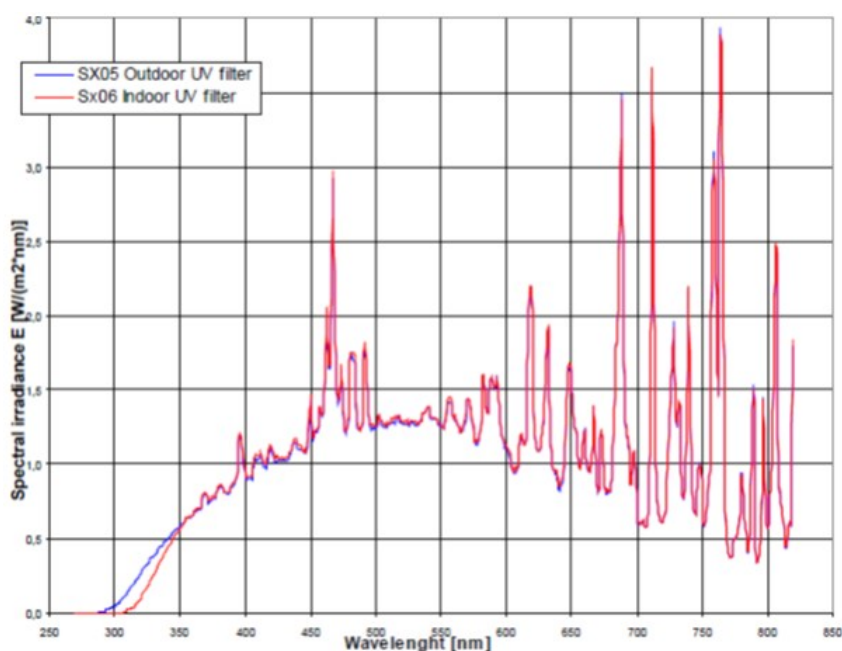


Figure S1: Emission of the Solar Box Xenon lamp with and without UV-filter. The photocatalytic experiments were performed without UV filter.

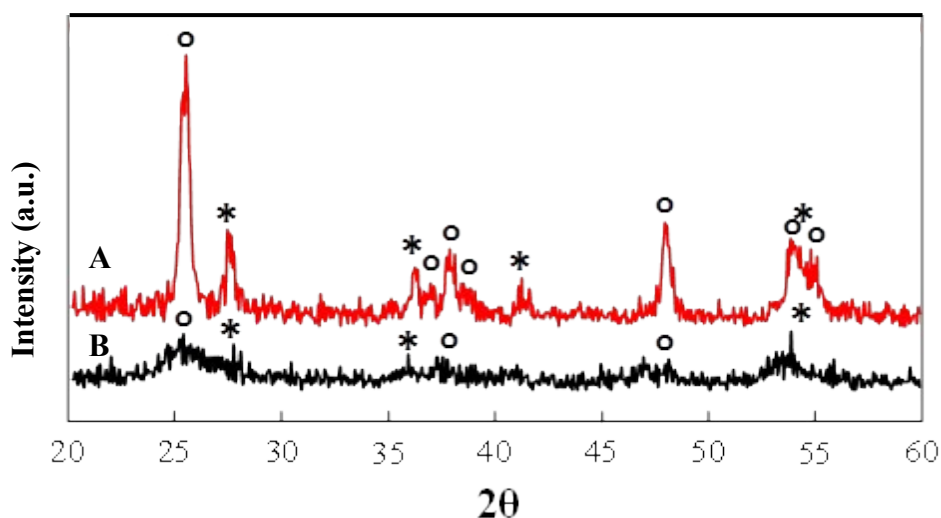


Figure S2: X ray diffraction patterns of HP05C (A) and HP05 (B) samples. Anatase (circles), Rutile (asterisks).

Table S1: Polymorphic phase, average micropore and mesopore widths, specific surface area, and particle size for HP05 and HP05C samples. A: Anatase, R: Rutile, BJH: Barrett-Joyner-Halenda method, BET: Brunauer-Emmet-Teller method.

Sample	Polimorphic phase*	Average micropore width (BJH, nm)	Average micropore width (BJH, nm)	Specific Surface Area (BET, m ² g ⁻¹)	Particle size (nm)
HP05	A: 7%	1.7	6.5	235	26
	R: 1%				
HP05C	A:44%	2.0	20.0	51	116
	R: 16%				

* The percentage of crystalline phases was determined with respect to a CaF₂ reference according to a method described in the literature.⁵²

References

- S1.** F. Parrino, V. Augugliaro, G. Camera-Roda, V. Loddo, M.J. López-Muñoz, C. Márquez-Álvarez, G. Palmisano, L. Palmisano, M.A. Puma, *J. Catal.* 2012, **295**, 254-260.
- S2.** H. Jensen, K.D. Joensen, J.-E. Jørgensen, J.S. Pedersen, E.G. Søggaard, *J. Nanopart. Res.* 2004, **6**, 519–526