Electronic Supplementary Information

Advances in photocatalytic NO_X abatement through the use of Fe₂O₃/TiO₂ nanocomposites

José Balbuena,^a Giorgio Carraro,^{b,*} Manuel Cruz,^a Alberto Gasparotto,^b

Chiara Maccato,^b Adrián Pastor,^a Cinzia Sada,^c Davide Barreca,^d and Luis Sánchez^{a,*}

- ^a Department of Inorganic Chemistry and Engineering Chemistry, Córdoba University, 14071
 Córdoba, Spain.
- ^b Department of Chemistry, Padova University and INSTM, 35131 Padova, Italy.
- ^c Department of Physics and Astronomy, Padova University and INSTM, 35131 Padova, Italy.
- ^d ICMATE-CNR and INSTM, Department of Chemistry, Padova University and INSTM, 35131 Padova, Italy.

^{*} Authors to whom correspondence should be addressed; E-mail: <u>giorgio.carraro@unipd.it; luis-</u> <u>sanchez@uco.es</u>.



Fig. S1. XRD diffraction patterns for bare Fe_2O_3 and for Fe_2O_3 -TiO₂ nanocomposites. Peak positions for *hematite* [Pattern N° 33-0664, JCPDS (2000)] and *anatase* [Pattern N° 021-1272, JCPDS (2000)] are marked by vertical bars.



Fig. S2. Surface XPS survey spectra of Fe₂O₃-TiO₂ nanocomposites.



Fig. S3. Plane view (a) and cross sectional (b) FE-SEM micrographs for a bare Fe_2O_3 deposit.



Fig. S4. Representative AFM micrographs for bare Fe_2O_3 and FeTi4 specimens. Calculated root-mean-square (RMS) roughness values for Fe_2O_3 and FeTi4 samples are 74 and 84 nm, respectively.



Fig. S5. Concentration profiles obtained for P25, TiO₂, Fe₂O₃ and FeTi4 samples during the photochemical degradation of gaseous NO under Vis light irradiation.



Fig. S6. Nitrogen oxide concentration profiles obtained for FeTi4 specimen under different utilization cycles.



Fig. S7. Simplified representation of the mechanism for PC activity enhancement occurring in Fe_2O_3/TiO_2 nanocomposites.

IR analysis

Infrared (IR) spectra were recorded by means of a Perkin Elmer FTIR System Spectrum BX, operating in transmittance mode at normal incidence.

The assignment of IR bands pertaining to Fig. S8 spectra is the following.

The band around 1640 cm⁻¹ corresponds to O–H bending vibrations, implying the presence of adsorbed water (Fig. S8a). The bands marked in Fig. S8b were assigned basing on to the previously reported information on the interaction of nitrogen oxides with TiO₂.¹⁻³ The bands located at 1529, 1506 and 1487 cm⁻¹ correspond to stretching vibrations of nitrate species^{1, 2, 4} whereas those at 1417 and 1261 cm⁻¹ are ascribed to nitrite ones.^{2, 4} The band at 1710 cm⁻¹ can be tentatively assigned to adsorbed NO₂.³ A more detailed attribution of IR bands attributed to N–O stretching vibrations of surface nitrate (NO₃⁻) and nitrite (NO₂⁻) species is a difficult task, since v(N–O) of different NO₃⁻ and NO₂⁻ species fall in the same 1700–1000 cm⁻¹ interval and their IR bands are strongly overlapped.¹



Fig. S8. IR spectra in the $1800 - 1200 \text{ cm}^{-1}$ range of (a) Fe₂O₃ and (b) FeTi4 samples before and after NO_X degradation tests.

References

- 1. R. V. Mikhaylov, A. A. Lisachenko, B. N. Shelimov, V. B. Kazansky, G. Martra and S. Coluccia, *J. Phys. Chem. C*, 2013, **117**, 10345-10352.
- 2. J. Sá and J. A. Anderson, *Appl. Catal. B*, 2008, 77, 409-417.
- B. Zhao, R. Ran, X. Wu, D. Weng, X. Wu and C. Huang, *Catal. Commun.*, 2014, 56, 36-40.
- 4. K. I. Hadjiivanov, *Catal. Rev.*, 2000, **42**, 71-144.