

W,N-doped TiO₂-anatase: a sunlight-operated catalyst for efficient and selective aromatic hydrocarbons photo-oxidation

Anna Kubacka,¹ Belén Bachiller-Baeza,¹ Gerardo Colón,^{2,*} Marcos Fernández-García¹

Instituto de Catálisis y Petroleoquímica, CSIC, C/Marie Curie 2, 28049-Madrid, Spain; Instituto de Ciencia de Materiales de Sevilla, CSIC, C/Américo Vespucio 49, 41092-Sevilla, Spain.

Catalyst preparation.

Materials were prepared using a microemulsion preparation method by addition of Titanium tetraisopropoxide to an inverse emulsion containing an aqueous solution (0.5 M) of ammonium tungsten oxide (Aldrich) or molybdate (Aldrich) dispersed in *n*-heptane, using Triton X-100 (Aldrich) as surfactant and hexanol as cosurfactant. Water/titanium and water/surfactant molar ratios were, respectively, 18 and 110 for all samples. The resulting mixture was stirred for 24 h, centrifuged, decanted, rinsed with methanol and dried at 298 K for 12h. Following the microemulsion preparation method, the solid precursors were subjected to a heating ramp in 8 v/v % NH₃/N₂ up to 723 K and treated at this temperature in 20 v/v % O₂/N₂ for 2 h. Reference systems with absence of N-containing species were also synthesized from the same precursors and subjected to the same thermal treatment but always in presence of oxygen (20 v/v % O₂/N₂).

Photo-catalytic Experimental Details

Gas phase photodegradation tests were carried out with two organic pollutants (toluene and styrene). Activity and selectivity for the gas-phase photooxidations were separately tested in a continuous flow annular photoreactor containing ca. 30 mg of photocatalyst as a thin layer coating on a pyrex tube. The corresponding amount of catalyst was suspended in 1 ml of water, painted on a pyrex tube (cut off at ca. 250 nm) and dried at RT. The reacting mixture (100 ml/min) was prepared by injecting toluene/styrene (Panreac, spectroscopic grade) into a wet (ca. 75 % relative humidity, RH) 20 vol. % O₂/N₂ flow before entering at room temperature to the photoreactor, yielding an organic inlet concentration of ca. 700 ppmv. Under such conditions, the reaction rate shows a zero order kinetics following a Langmuir-Hinshelwood mechanism with respect to the total flow and organic pollutant/oxygen concentrations.

After flowing the mixture for 6 h (control test) in the dark, the catalyst was irradiated by four fluorescent daylight lamps (6W, Sylvania F6W/D) with a radiation spectrum simulating sunlight (UV content of 3 %; main emission lines at 410, 440, 540, and 580 nm), symmetrically positioned outside the photoreactor. Reaction rates were evaluated (vide supra) under steady state conditions, typically achieved after ca. 3-6 h (depending on the reaction) from the irradiation starting. No change in activity was detected for all samples within the next 48 h. The concentration of reactants and products was analyzed using an on-line gas chromatograph (Agilent GC 6890) equipped with HP-PLOT-Q/HP-Innowax columns (0.25 mm I.D. x 30 m) and TCD/FID detectors.

Characterization Experimental details

Ti:M composition was analyzed by using inductively coupled plasma and atomic absorption (ICP-AAS), while BET surface areas were measured by nitrogen physisorption (Micromeritics ASAP 2010). XRD patterns were recorded in the range $10^\circ < 2\theta < 120^\circ$ using 0.02° steps. X-ray diffraction (XRD) patterns were obtained using a Siemens D-501 diffractometer with Ni filter and graphite monochromator with a Cu K_α X-ray source. DRIFTS spectra were acquired with a Bruker Equinox FT55 equipped with an MCT detector cooled with liquid N_2 . UV-visible diffuse reflectance spectroscopy experiments were performed with a Shimadzu UV2100 apparatus with a nominal resolution of ca. 1 nm using $BaSO_4$ as reference.

The microcalorimetric studies of ammonia adsorption were carried out in a differential heat-flow microcalorimeter (Tian-Calvet type C80; Setaram) connected to a conventional volumetric apparatus. The adsorption temperature was maintained at 353 K in order to limit physisorption. Each sample was evacuated overnight at 423 K and cooled to adsorption temperature under vacuum. Equilibrium pressure was measured by means of a Baratron pressure transducer MKS Instrument.

XPS experiments were performed in a standard UHV chamber (base pressure 3×10^{-9} Torr) equipped with a 100 mm hemispherical electron analyzer (Scienta, SES 100). Mg K_α radiation ($h\nu = 1253.6$ eV) was used to acquire the core level spectra (O 1s, N 1s, Ti 2p, Mo 3d, W 4d). The powder samples were smeared on a carbon tape and the binding energy is referenced to the C 1s peak at 284.6 eV from the carbon tape.

Fig. S1. XRD spectra of the samples.

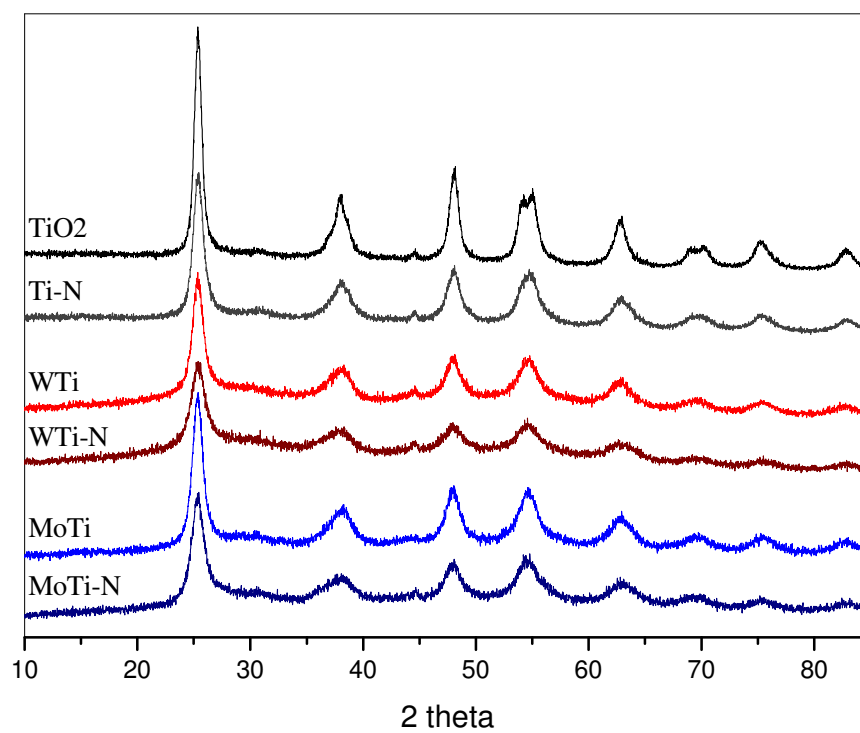
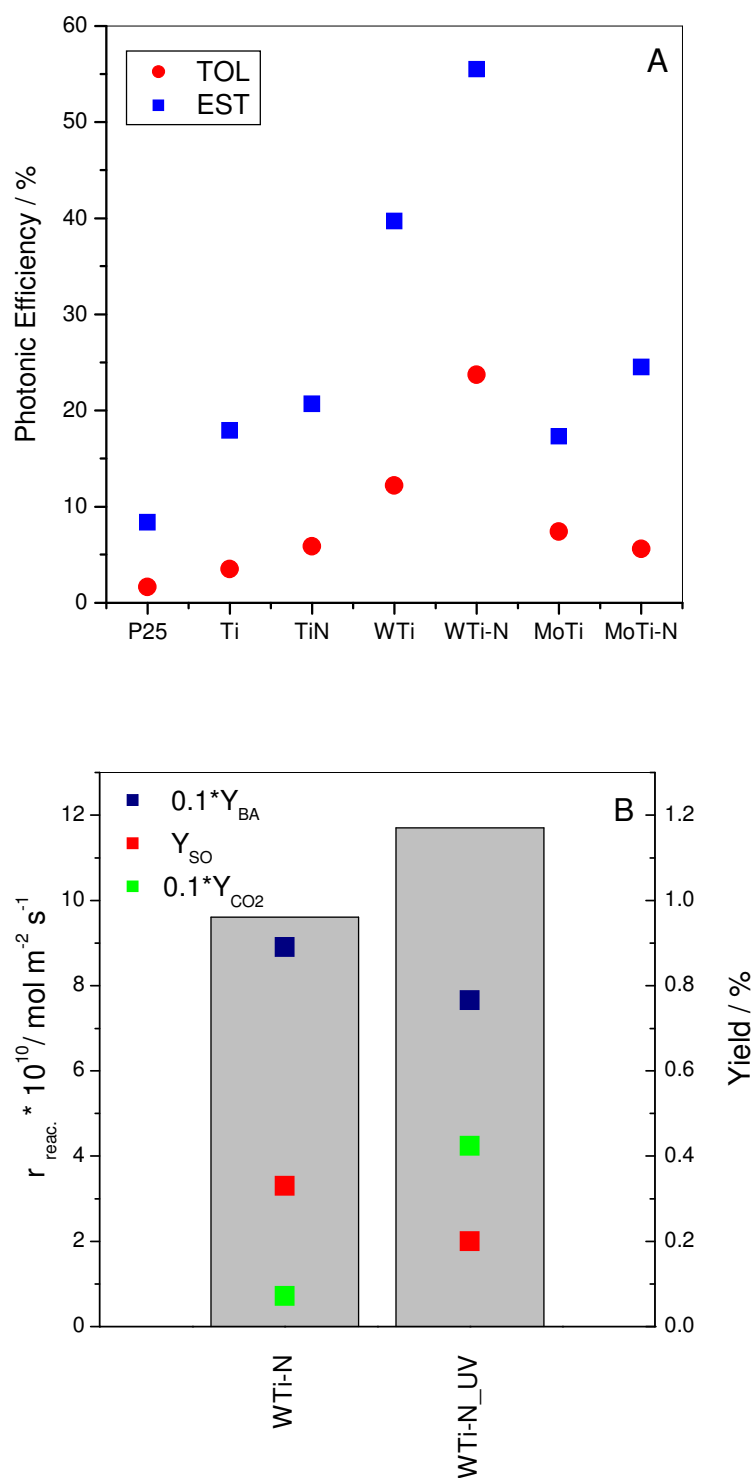


Fig. S2. (A) Photonic efficiency for toluene and styrene photo-oxidation. (B) TiW-N reaction rates for styrene photo-oxidation using sunlight and pure UV light (365 nm).



Photonic efficiency was calculated as the ratio between the reaction rate (mol s^{-1}) and the rate of photons absorbed by the system (einstein s^{-1}).

Fig. S3. (A) UV-visible spectra of the samples; (B) plot allowing band gap estimation considering the oxides indirect gap semiconductors.

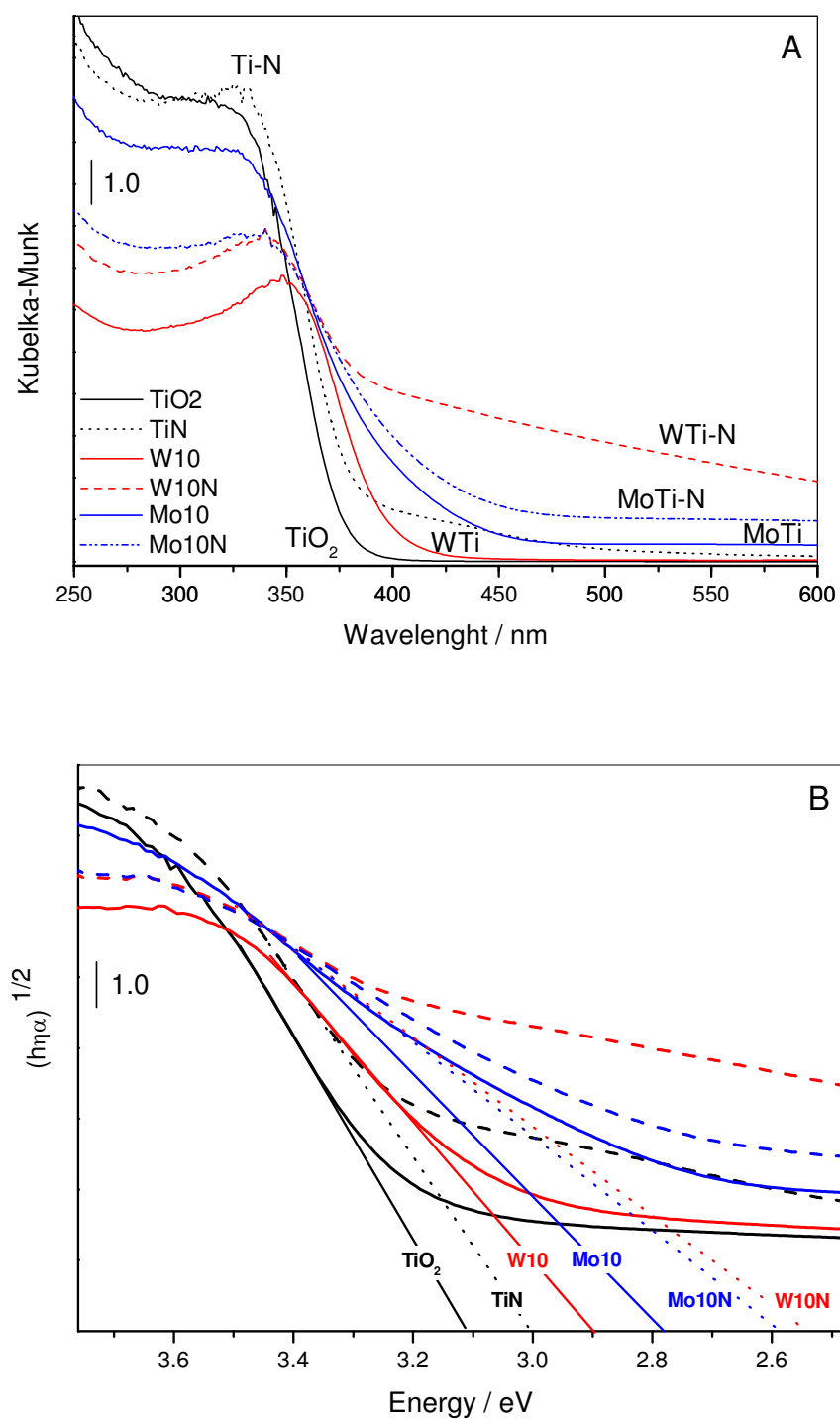
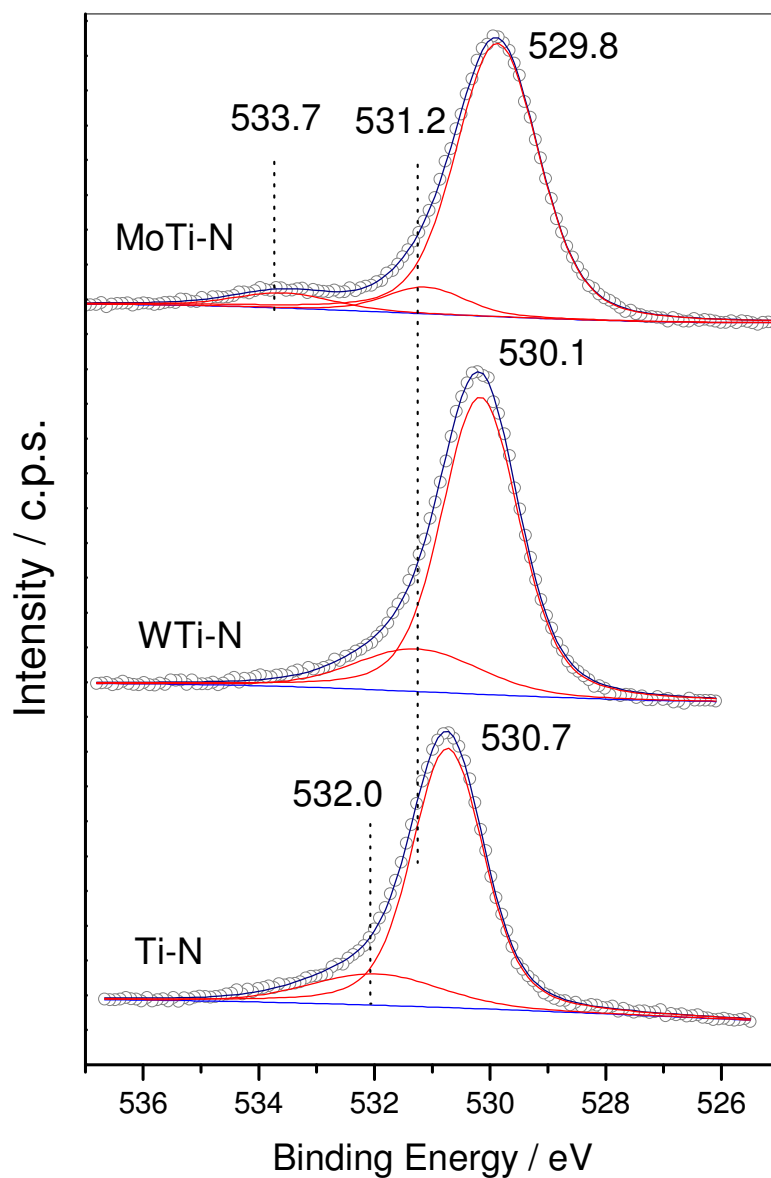
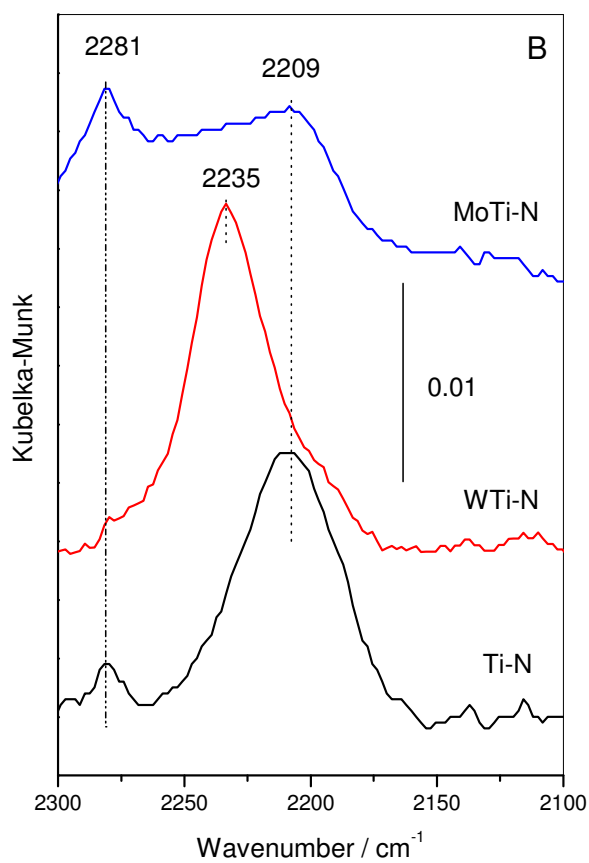
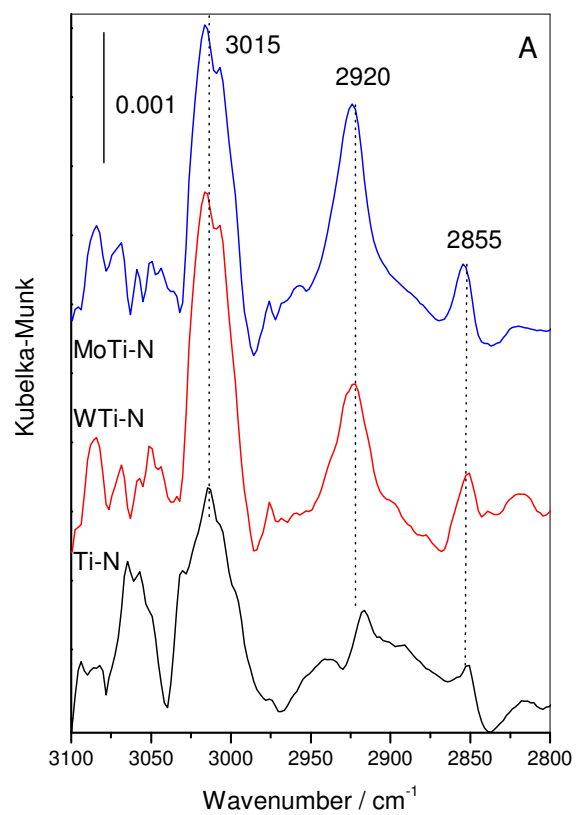


Fig. S4. O 1S XPS peak for N-containing samples.



As detailed in ref. 7; ca. 530/531 eV contributions correspond, respectively, to lattice and surface (OH) anatase ions while the 533.7 eV peak correspond to O ions with binding energy characteristic of Mo(VI) oxide. Note that a similar contribution is absent in WTi-N

Fig. S5. Background-substrated difference DRIFTS spectra of samples. Difference spectra are obtained by subtracting the MTi reference signal from the corresponding MTi-N spectrum.



Plot A shows low intensity peaks ascribable to NH_x (and residual CH_x ; 2920 cm^{-1}) species while plot B displays contributions exclusively ascribable to $(\text{CN})^n$ type species (see ref. 12 of main text for details). In Fig. S4-B, peak at 2281 cm^{-1} appears in both MoTi-N and MoTi spectra and cannot be ascribed to a N-containing species.