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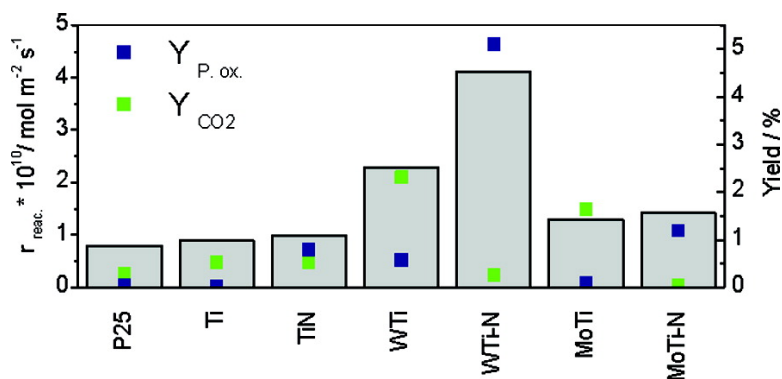
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W,N-Codoped TiO₂-Anatase: A Sunlight-Operated Catalyst for Efficient and Selective Aromatic Hydrocarbons Photo-Oxidation

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New W,N-doped TiO₂ anatase-based materials are synthesized having both unprecedented high activity and selectivity in the gas-phase partial oxidation of aromatic hydrocarbons using sunlight as excitation energy and molecular oxygen as oxidant.

Recent research has shown that titanium(IV) oxide (TiO₂) photocatalysts display excellent activity for a number of industrially useful reactions oriented to the synthesis of fine chemicals.¹ Nowadays, society demands increasingly stringent regulations that open up opportunities for novel green photocatalytic routes leading to the substitution/modification of TiO₂, an ultraviolet (UV) absorber, in order to allow the use of sunlight as the energy source of fine chemical production processes.² This last goal requires the use of visible light photons but also an adequate overall handling of UV–vis radiation as a significant number of new photocatalysts do perform adequately under visible light but typically display poor performance with respect to TiO₂ commercial references (e.g., Degussa P25) under sunlight. This is due to an unfavorable balance between the enhanced visible light absorption and a negative impact on charge recombination.³ In this letter, we propose the bulk modification of TiO₂ by metal–nitrogen codoping as a route for the selective oxidation of aromatic hydrocarbons to either aldehyde derivatives with wide use in the flavor, confectionary, and beverage industries, or to epoxides with application in plastic industries.⁴ Our approach aims to use sunlight and air (e.g., molecular oxygen) for both economical and environmental reasons and considers a gas-phase scheme to ensure a reasonable catalysts stability and the absence of recovery steps typical of liquid-phase reactions.^{1–4} It is interesting to remark that the proposed formulation constitutes a novel photocatalytic material for fine chemistry synthesis with notable structural differences with isolated cation materials (Ti, Cr, Pd, etc.)^{1,5} or size-restricted, partially amorphous TiO₂-based or composite catalysts (TiO₂/MCM, TiO₂/clays, etc.).^{1,4,6}

M (M = W, Mo)–Ti containing solid precursors were prepared following a microemulsion method previously described (see Supporting Information for details).⁷ The M–Ti and Ti solid precursors were subjected to a heating ramp in 8 v/v % NH₃/N₂ up to 723 K and treated for 2 h at this temperature in 20 v/v % O₂/N₂. Reference systems were also synthesized

TABLE 1: Main Physico-Chemical Parameters

sample	M (at %) ^a ICP-AAS/XPS	N (at %) ^a ICP-AAS/XPS	BET (m ² g ^{−1})	size (nm)	apparent band gap (eV) ^b
Ti			105	10.4	3.1
Ti–N		0.1/0.5	160	7.6	3.0
MoTi	11.1/13.0		153	7.4	2.75
MoTi–N	11.2/13.1	0.2/2.0	106	6.2	2.6
WTi	10.2/10.0		143	7.2	2.9
WTi–N	10.4/8.9	0.3/1.5 ^c	156	5.7	2.55

^a Data for chemical analyses (ICP-AAS) followed by XPS measurements (see Supporting Information). ^b Data considering the oxides indirect gap semiconductors (see Supporting Information, Figure S3). ^c Peak integration is considered semiquantitative by effect of the dominant Mo 3p peak overlapping.

from the same precursors but subjected to a isothermal treatment (723 K; 2 h) in 20 v/v % O₂/N₂. W and Mo were selected as they form anatase-based substitutional mixed oxides with a reasonable homogeneity up to ca. 10–15 at % and display excellent photoactivity in hydrocarbon mineralization reactions under sunlight excitation.⁷ Chemical analyses and main physicochemical properties of the synthesized materials are summarized in Table 1.

We obtained high surface area materials (100–150 m² g^{−1}) with primary particle size below 10 nm, which appears to decrease moderately upon ammonia treatment. The XRD and Raman characterization (Supporting Information, Figure S1) detected the dominant presence of the anatase polymorph in all samples, together with a small fraction of brookite (only visible by Raman). The process performance was followed by measuring the aromatic hydrocarbons (toluene, styrene) and product(s) concentrations and calculating substrate conversion and yield toward partial and total (CO₂) oxidation products. Absence of photolysis and significant polymerization (the latter in the styrene case) was checked in blank tests. Stability of reported observables was checked for 48 h of continuous use. Presence of Mo and W on anatase improves the performance of TiO₂ reference systems in the photo-oxidation of toluene/styrene (Figure 1 and Supporting Information, Figure S2). This confirms previous data on toluene.⁷ Figure S2 in Supporting Information also shows that pure UV light increases the CO₂ yield, indicating that partially oxidation products are favored in the case of

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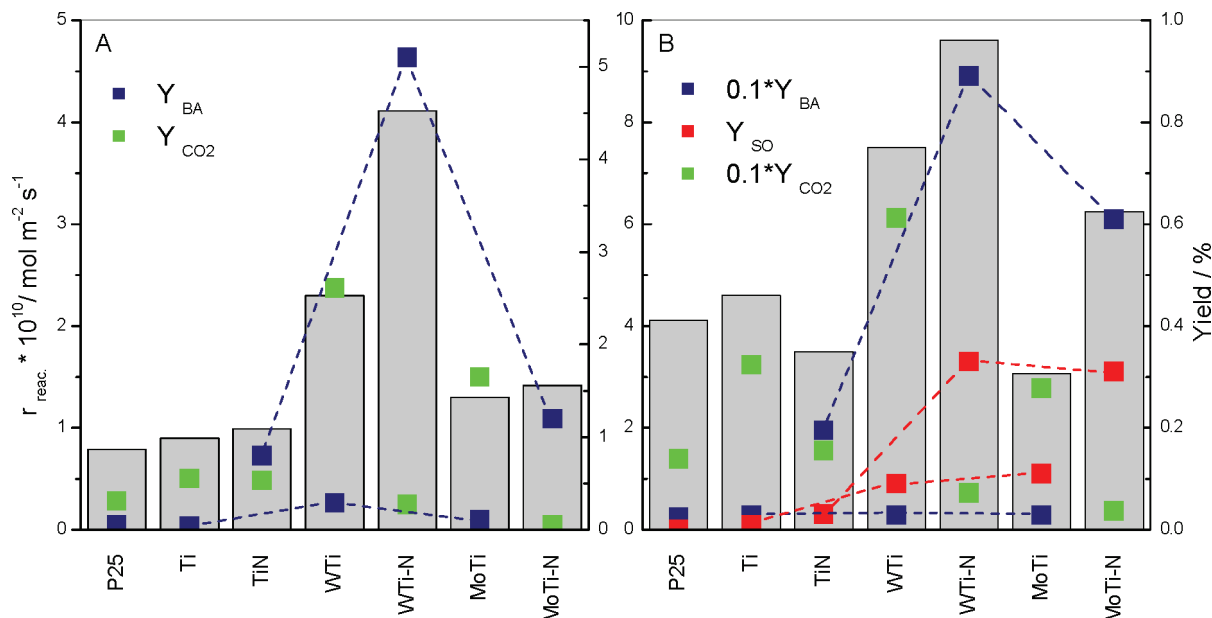


Figure 1. Experimental results for (A) toluene and (B) styrene photo-oxidation. BA and SO stand for, respectively, benzaldehyde and styrene oxide.

visible-light excitation. Figure 1 indicates that WTi and MoTi are essentially total oxidation catalysts, displaying CO_2 as the main reaction product. The treatment with ammonia alters significantly the behavior of the anatase-type materials. First, it enhances the reaction rate, particularly for WTi, and second it modifies profoundly its selectivity. In the case of toluene, both WTi-N and MoTi-N samples give predominantly benzaldehyde. A slightly lower selectivity (90 vs our 95%) has been previously reported for P25 in water (liquid-phase) under UV light.⁸ Styrene photooxidation yielded two main products; benzaldehyde (plus acetaldehyde) and styrene oxide. The yield to styrene oxide is maximized for the WTi-N sample. Comparison with previous reports indicates the significantly low CO_2 production displayed by both M,N-codoped materials.^{4b,8,9} The combination of a high reaction rate and a near complete selectivity to partial oxidation products appears however a distinctive feature of our W,N-doped TiO_2 -anatase system, not matched by any other sample here studied or previously reported.^{1,2,4,5,7-9}

The ammonia treatment favorably alters selectivity for Ti and Mo-Ti systems and both activity and selectivity for W-Ti. The rationalization of this behavior can be discussed on the basis of a combination of two potentially important effects; a change in surface acidity and of the structural/electronic properties of the anatase phase. NH_3 calorimetry data (Figure 2) show an increase of acidity by ammonia treatment in the case of Ti and Mo-Ti series but not on W-Ti, indicating that surface modification may play a role (likely connected with reactant, hydrocarbon adsorption) in the first two systems behavior but not on W-containing ones. In the last case, W by itself strongly promotes acidity with respect to bare P25/Ti but the combination of N and W does not further increase acidity. Surface modification may thus play a role on WTi versus the Ti reference samples but not for WTi-N with respect to WTi. The success of the W,N combination seems thus grounded in other factors among which the coupled combination of the band gap modification and the maintenance of the structural ordering at the anatase structure appears as capital. Supporting Information, Figure S3 displays the optical absorption spectra of the samples and Table 1 summarizes their apparent band gap (assuming the oxides are

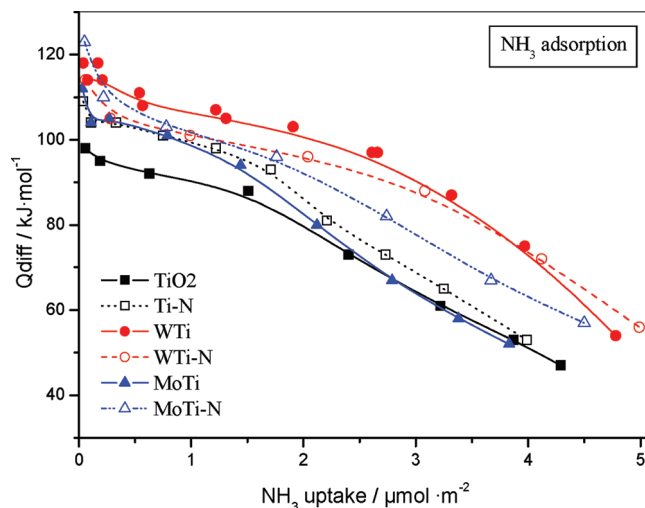


Figure 2. NH_3 isotherm adsorption profiles.

indirect gap semiconductors).² While WTi and MoTi decrease the anatase apparent band gap by, respectively, ca. 0.2 and 0.4 eV, allowing visible-light absorption, their reaction rates comes out from a trade off between the enhancement of visible light absorption and the increasing electron-hole recombination with respect to Ti. As previously shown in ref 7, presence of Mo-rich entities within the anatase structure makes the second fact preponderant up to produce just a moderate increase of the rate with respect to the parent Ti sample. W samples display however a truly substitutional disordered anatase-type mixed oxide with exclusive presence of heteroatom (W-O-Ti) bonds¹⁰ and improved light to chemical energy conversion. As demonstrated by the O 1s peak (Supporting Information, Figure S4), MoTi-N shows the presence of heteroatom-rich zones characteristic of Mo-Ti samples (e.g., contribution at ca. 533.7 eV)⁷ while these are absent in WTi/WTi-N. In addition, MoTi-N has an essentially unaffected band gap while there is a ca. 0.3–0.4 eV decrease for WTi-N with respect to the MoTi/WTi counterparts. The joint consideration of these factors would thus explain the rate variations observed with respect to Ti or MTi references. While in MoTi-N and Ti-N samples surface acidity can justify

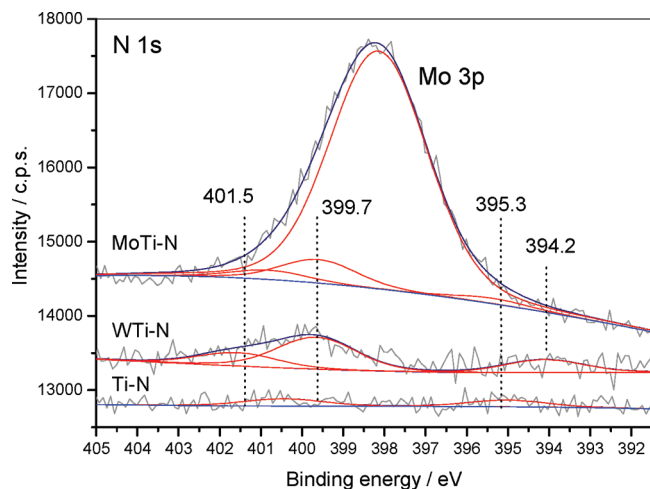


Figure 3. N 1s XPS spectra for N-containing samples.

a modest activity modification with respect to their parent systems, WTi-N activity increase is mostly ascribed to a modification of the band gap while maintaining the optimal anatase structural properties (absence of W-rich zones within the anatase structure) that would limit electron-hole recombination.

The change in selectivity is more difficult to interpret but some clues can be extracted from the XPS data present in Table 1. Ammonia treatment modestly modify M cation surface concentration (e.g., small depletion of W and enrichment of Mo) from the surface and yields an increasing N-concentration (both at surface and bulk) in the order $\text{Ti-N} < \text{MoTi-N} < \text{WTi-N}$. At the N 1s region, we detected (Figure 3) two contributions at ca. 399.7/401.5 eV^{2,11} which can be easily correlated with, respectively, IR-detected $(\text{NH}_x)^{n+}$ and $(\text{CN})^{n-}$ type species (Supporting Information, Figure S5).¹² Codoping modestly enhances the amount of the two species (Figure 3) but mainly alters the chemical bond of $(\text{CN})^{n-}$ species to the anatase network in the W-Ti case. The modification of the surface altering selectivity seems however characteristic of the ammonia treatment and only modestly dependent on the nature of the sample (although copresence of M and N decreases CO_2 yield significantly). Differences among samples could be thus due to the different nature of the dominant $(\text{CN})^{n-}$ species (Supporting Information, Figure S5). The XPS also showed the presence of Metal-N bonds in Ti-N and MoTi-N samples (binding energy 395.4 eV) and of W-N for WTi-N (394.2 eV) but in very low quantities, indicating their probable limited influence in the photochemical process.^{2,11} This requires however further analysis.

Summing up, this letter presents a W,N-doped TiO_2 anatase-based material having both high activity (2–4 times P25, Ti,

Ti-N references) and selectivity in aromatic hydrocarbons partial oxidation to fine chemical oxygenates using sunlight as the energy source of the process. This behavior is exclusive of the system and not obtained in similar Mo,N codoped materials which lack an effective rate enhancement. The experiments point out the synergistic W-N effect on the band gap (ca. 0.6 eV decrease) as well as some specific characteristics of N-containing surface species as key parameters to optimize activity and the yield to oxygenate compounds. The nature of the N-containing species and W-N interaction as well as other potentially important variables (as primary particle size, etc.) on catalytic activity require however further study.

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Supporting Information Available: Experimental details and data concerning reaction activity/selectivity and XRD, UV-vis, XPS, and infrared spectroscopies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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