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Individual effect of charge balance defects on the photocatalytic activity of Cr^{3+}-modified TiO_2

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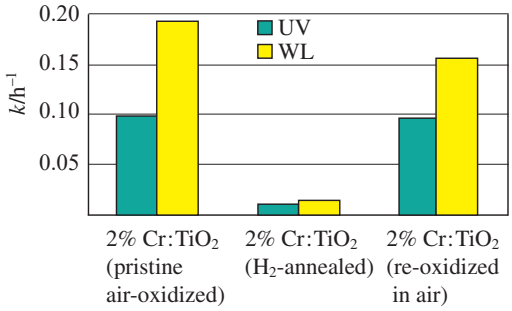
Loss in the photocatalytic activity of Cr^{3+}:TiO_2 powders upon hydrogen annealing shows that charge-compensating oxygen vacancies V_O and Cr^{6+} ions can have opposite effects on the kinetics of photocatalytic decolorization of methyl orange solution. The former ones inhibit this reaction acting as electron–hole recombination centers, and the latter ones promote it playing the role of active sites. This conclusion is verified by an XPS technique for a Cr^{3+}-doped TiO_2 sample and by ^{121}Sb Mössbauer spectroscopy for a co-doped (Cr^{3+},Sb^{5+}):TiO_2 sample.



The Cr^{3+}-doped TiO_2 powders are promising materials for solar energy conversion.[1,2] It was established that doping with Cr^{3+} leads to the formation of energy levels in the gap of this semiconductor, which allow it to absorb visible light, by contrast to undoped TiO_2 capable of absorbing only in the UV region. However, it was found that Cr^{3+} doping can completely deactivate this catalyst under both UV and visible light irradiation.[3] This negative effect was attributed to the formation of charge-balancing V_O oxygen vacancies and Cr^{6+} ions, which act as (e^-,h^+) recombination centers towards photogenerated electrons and holes.[4] While the suggested deactivation mechanism appeared consistent with the recovery of catalytic activity upon co-doping with Sb^{5+}, certain peculiarities of the co-doped (Cr^{3+},Sb^{5+}):TiO_2 samples remained unclear, and the individual impact of V_O and Cr^{6+} was not characterized.

Thus, to clarify the individual effect of either V_O or Cr^{6+}, variations in the photocatalytic activity of Cr^{3+}-doped TiO_2 induced by hydrogen annealing should be considered. In fact, such a reducing thermal treatment being only capable of increasing the V_O content and, by contrast, decreasing the Cr^{6+} content, this experiment would allow one to evaluate the effect of either of these point defects. For this purpose, we investigated the decolorization of aqueous solutions of methyl orange (MO) in the presence of single-phase Cr^{3+}-doped anatase TiO_2 powders under either UV or white light (WL) irradiation. The sample of Cr^{3+}:TiO_2 **1** was obtained by the annealing of co-precipitated $Ti(OH)_4$ and $Cr(OH)_3$ in air (for 2 h at 500 °C). The sample of Cr^{3+}:TiO_2 **2** was obtained by the annealing of undoped anatase powder wetted with aqueous solution of NH_3, impregnated with the required amount of $CrCl_3$ solution, and finally calcined in air (for 2 h at 500 °C) under the same conditions. The sample of (Cr^{3+},Sb^{5+}):TiO_2 was obtained by annealing the relevant co-precipitated hydroxides in air. The chromium concentration [Cr^{3+}] = 2 at% was chosen to compare the available data[3] on both Cr^{3+}-doped and (Cr^{3+},Sb^{5+}) co-doped rutile TiO_2 photocatalysts. To prepare (Cr^{3+},Sb^{5+}):TiO_2, we took into account a very limited solubility of Sb^{5+} ions (lower than 1 at%) in 3d oxides. The quantity of antimony [Sb^{5+}] = 0.6 at% used to synthesize (Cr^{3+},Sb^{5+}):TiO_2 allowed us to reliably determine the valence state(s) of this dopant using ^{121}Sb Mössbauer spectroscopy[5].

To compare the photocatalytic activities, we used the decolorization reaction rate constants k. Prior to irradiation, a cuvette containing 10 mg of catalyst powder and 1.5 ml of MO solution was centrifuged to form a firm catalyst layer at the bottom. Irradiations

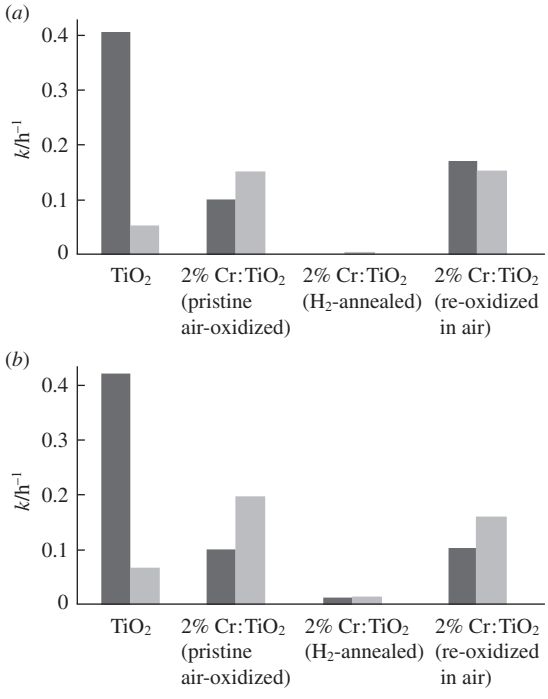


Figure 1 Constants k of the decolorization rate of MO in the presence of samples (*a*) **1** and (*b*) **2** annealed in different gaseous atmospheres. Dark grey and light grey columns represent the data obtained under UV and WL irradiation, respectively.

were carried out using a LED (UV, λ = 370 nm or WL, color temperature T_c = 6500 K) installed underneath of the cuvette. The optical density at λ = 460 nm was determined in the cuvette used for irradiation. Kinetic curves used to calculate k were correctly approximated by a linear equation of first-order reactions.

Comparison of the decolorization kinetics in the presence of Cr^{3+}:TiO_2 **1**, Cr^{3+}:TiO_2 **2** and TiO_2 reference sample shows that Cr^{3+} doping slowed down the reaction under UV irradiation and accelerated it under WL irradiation (Figure 1).

The activity of Cr^{3+}-doped TiO_2 powders in the test reaction allowed us to evaluate the effect of hydrogen annealing on the decolorization efficiency and, consequently, to assess the individual impact of V_O and Cr^{6+}. For this purpose, reference TiO_2, Cr^{3+}:TiO_2 **1** and Cr^{3+}:TiO_2 **2** were annealed in hydrogen for 1 h at 300 °C. This thermal treatment did not significantly affect the value of k in the presence of reference TiO_2, but it drastically decreased the photocatalytic efficiency of Cr^{3+}-doped samples. Consequently, this experiment has shown that Cr^{6+} ions, expected to disappear upon hydrogen annealing, behaved as catalytically active centers while V_O vacancies, by contrast, inhibited the studied reaction. This conclusion was confirmed by the recovery of photocatalytic activity of either Cr^{3+}:TiO_2 **1** or Cr^{3+}:TiO_2 **2** observed after annealing in air (see Figure 1). Finally, the anticipated correlation between the values of k and Cr^{6+} content was clearly demonstrated by the evolution of the Cr $2p_{3/2}$ XPS spectra of Cr^{3+}:TiO_2 **2** annealed under different gas atmospheres (Figure 2). Whereas the contribution of the spectral component assignable to Cr^{6+} (binding energy E_b = 579.6 eV)[6] could not be evaluated in Cr^{3+}:TiO_2 **1** because of a much lower Cr concentration in the surface layers of this catalyst obtained using co-precipitated hydroxides, similar changes in the photocatalytic activity of Cr^{3+}:TiO_2 **1** and Cr^{3+}:TiO_2 **2** induced by hydrogen annealing

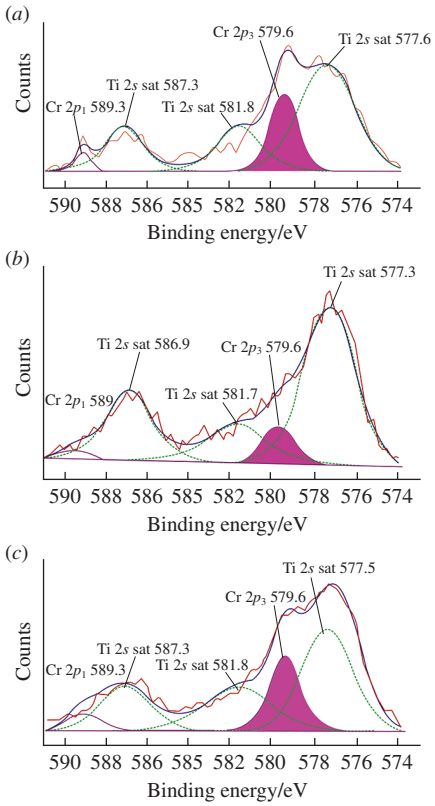


Figure 2 Evolution of Cr^{VI} contribution (shaded spectral component, E_b = 579.6 eV) in Cr $2p_{3/2}$ XPS spectra of sample **2**: (*a*) in the initial state, (*b*) after H_2 annealing, and (*c*) after subsequent reoxidation. Dotted curves represent Ti 2*s* satellites of the main Ti $2p_{3/2}$ spectral component (E_b = 458.8 eV).

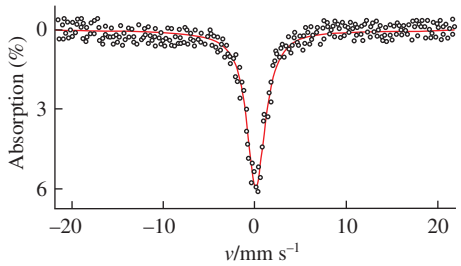


Figure 3 ^{121}Sb Mössbauer spectrum of the (2 at% Cr^{3+} + 0.6 at% Sb^{5+}):TiO_2 sample annealed in air at 500 °C for 2 h.

show that they have the same origin. However, to quantify the relationship between the XPS spectra of the title catalyst and the kinetics of the test reaction, further experimental work is needed.

Thus, we found that V_O vacancies and Cr^{6+} ions exerted opposite effects on the catalyst activity in the test reaction. To analyze the changes resulting from the insertion of Sb^{5+} ions into Cr^{3+}:TiO_2, which are capable of suppressing the formation of both V_O and Cr^{6+}, catalytic measurements were performed with (2 at% Cr^{3+} + 0.6 at% Sb^{5+}):TiO_2, and they have shown that its photocatalytic activity remained almost the same as that of 2 at% Cr^{3+}:TiO_2 **1**. It was suggested[3] that a decrease in the modifying efficiency of the Sb^{5+} dopant could result from the auto compensation of its excess of charge (according to the reaction scheme Sb^{5+} + Sb^{3+} substitute $2Ti^{4+}$) due to partial reduction of Sb^{5+} to Sb^{3+}. To verify this suggestion in the case of (2 at% Cr^{3+} + 0.6 at% Sb^{5+}):TiO_2, we measured the ^{121}Sb Mössbauer spectrum (Figure 3). This spectrum contains the only peak characterized by the isomer shift δ close to 0 mm s^{-1}, which implies the presence of antimony in the 5+ oxidation state. Consequently, the observed incapability of Sb^{5+} ions to suppress the formation of either V_O or Cr^{6+} in the studied sample was not due to the auto compensation by Sb^{3+} ions (δ ~ –12 mm s^{-1})[5] but reflected an independent charge-balance mechanism for the Sb^{5+} dopant, for instance, by the formation of Ti^{4+} vacancies. Such a mechanism was reported for isoelectronic Sn^{4+} ions in Cr_2O_3.[7] In this antiferromagnetic compound, the spin polarization of Sn^{4+} by neighboring Cr^{3+} ions resulted in the magnetic hyperfine splitting of the ^{119}Sn Mössbauer spectrum whose analysis has revealed, for certain Sn^{4+} ions, the lack of one magnetic neighbor Cr^{3+}.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.11.041.

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