

## Effect of $\text{Sb}^{5+}$ codopant ions on the ultraviolet photocatalytic activity of $\text{Fe}^{3+}$ -modified anatase

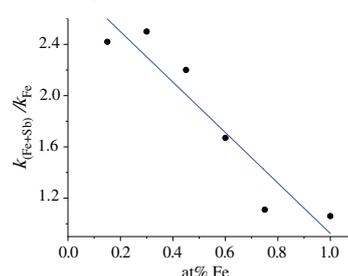
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The presence of antimony in ( $x$  at%  $\text{Fe}^{3+}$  +  $x$  at%  $\text{Sb}^{5+}$ ): $\text{TiO}_2$  powder samples containing equimolar amounts ( $0.15 \leq x \leq 1$ ) of the dopant cations was accompanied by an increase in the reaction rate constant  $k$  of the decolorization of methyl orange. Nevertheless, the increase in the rate of this test reaction, consistent with a decrease in the number of charge balance oxygen vacancies  $V_{\text{O}}$  imputable to the codoping with  $\text{Sb}^{5+}$ , rapidly weakened with increasing  $x$ . This effect is accounted for by the increased number of  $\text{Fe}^{3+}$ - $V_{\text{O}}$  associates slowing down the outward diffusion of  $V_{\text{O}}$  vacancies and, consequently, their rate of annealing in the studied catalyst.

Drop in efficiency of the equimolar ( $\text{Fe}^{3+}$  and  $\text{Sb}^{5+}$ )-codoping upon increasing the iron concentration



**Keywords:** ( $\text{Fe}^{3+}$ ,  $\text{Sb}^{5+}$ )-codoped anatase  $\text{TiO}_2$ , photocatalytic activity, decolorization of methyl orange, charge balance mechanism, oxygen vacancies,  $^{57}\text{Fe}$  Mössbauer spectra.

Although  $\text{TiO}_2$ -based photocatalysts are successfully used in various processes, their functional properties are poorly understood.<sup>1–5</sup> The doping of titania with  $\text{Cr}^{3+}$  ions allows it to absorb visible light and thus improves its efficiency for solar energy conversion. However, this doping can completely deactivate this catalyst under irradiation with UV and visible light. This undesirable effect, which was observed in a reaction of oxygen evolution from an  $\text{AgNO}_3$  solution in the presence of  $\text{Cr}^{3+}$ -doped rutile, was attributed to the formation of oxygen vacancies  $V_{\text{O}}$  and  $\text{Cr}^{6+}$  ions, the charge compensating point defects that act as ( $e^-$ ,  $h^+$ ) recombination centers towards photogenerated electrons ( $e^-$ ) and holes ( $h^+$ ).<sup>6</sup> The suggested deactivation mechanism was consistent with the partial restoration of catalytic activity upon codoping with  $\text{Sb}^{5+}$ ; however, it required a significantly larger amounts of antimony to compensate the positive charge deficiency of the  $\text{Cr}^{3+}$  ions. Such a behavior of antimony was due to either the autocompensation of  $\text{Sb}^{5+}$  ions by their partial reduction to  $\text{Sb}^{3+}$  or the volatility of antimony oxides under annealing conditions.<sup>6</sup> The effect of the  $\text{Sb}^{5+}$  codopant was even more feeble in the photocatalytic decolorization reaction of methyl orange (MO).<sup>7</sup> The  $^{121}\text{Sb}$  Mössbauer spectra clearly demonstrated both the presence of antimony only in a pentavalent state and the consistence of the intensity of resonant absorption with the amount of antimony used for the synthesis.<sup>7</sup> Hence, in this case, the inability of  $\text{Sb}^{5+}$  ions to affect the photocatalytic activity in an expected manner obviously cannot be due to their autocompensation; it pointed to either their independent charge balance mechanism or a much lower solubility in the  $\text{TiO}_2$  lattice, as compared to the number of present  $\text{Cr}^{3+}$  ions. Taking into account the widespread use of  $\text{Sb}^{5+}$  ions in various heterovalent substitutions, we studied the photocatalytic activity of a series of  $\text{TiO}_2$  powder samples containing variable equimolar amounts of

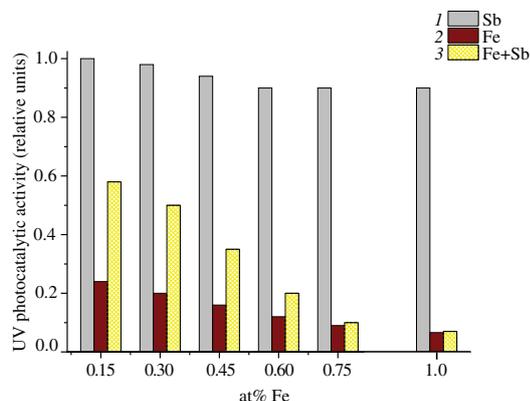
$\text{Fe}^{3+}$  and  $\text{Sb}^{5+}$  ions in the decolorization reaction of MO in solutions. The choice of  $\text{Fe}^{3+}:\text{TiO}_2$  as a matrix for studying the effect of the  $\text{Sb}^{5+}$  codopant was suggested by the reported  $^{57}\text{Fe}$  Mössbauer spectrum of  $\text{TiO}_2$  doped with 2 at%  $\text{Fe}^{3+}$ , which evidenced the presence of iron in its pristine trivalent state.<sup>8</sup> Thus, the  $\text{Fe}^{3+}$  charge deficit could be balanced only by oxygen vacancies in contrast to that in  $\text{Cr}^{3+}:\text{TiO}_2$ , where both  $V_{\text{O}}$  and  $\text{Cr}^{6+}$  ions were involved in the  $\text{Cr}^{3+}$  charge balance mechanism. Consequently, the Fe-doped samples allowed us to directly relate the  $\text{Fe}^{3+}$  content to the  $V_{\text{O}}$  content and to assess the number of  $V_{\text{O}}$  caused by  $\text{Sb}^{5+}$  codoping by measuring the ultraviolet photocatalytic activity of the relevant samples.

The results presented here were obtained using single-phase anatase  $\text{TiO}_2$  powders.<sup>†</sup> To compare the photocatalytic activities, we used the decolorization reaction rate constants  $k$ . Irradiations were carried out using a LED ( $\lambda = 370$  nm,  $P = 3$  W).<sup>‡</sup> Optical density was determined at  $\lambda = 460$  nm, and the values of  $k$  were calculated using a linear equation of first-order reactions.

Figure 1 shows the results of photometric measurements performed in a series of ( $x$  at%  $\text{Fe}^{3+}$  +  $x$  at%  $\text{Sb}^{5+}$ ): $\text{TiO}_2$  samples containing variable equimolar amounts of two modifying cations along with those obtained in monodoped  $x$  at%  $\text{Fe}^{3+}:\text{TiO}_2$  and  $x$  at%  $\text{Sb}^{5+}:\text{TiO}_2$  samples. The  $\text{Fe}^{3+}$  monodoping, which is responsible for the formation of  $V_{\text{O}}$ , resulted in a drastic decrease in  $k_{\text{Fe}}$ , as compared to the value of  $k_0$  observed in reference  $\text{TiO}_2$ .<sup>8</sup> The  $\text{Sb}^{5+}$  monodoping also somewhat decreased the value

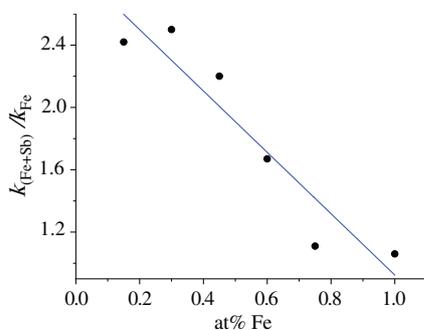
<sup>†</sup> The samples were synthesized by annealing the precursors, which were prepared by coprecipitation of analytical-grade hydroxides, in air at 500 °C for 2 h.<sup>8</sup>

<sup>‡</sup> Before irradiation, a cuvette containing 5 mg of a catalyst and 1 ml of a solution of MO was centrifuged to form a firm catalyst layer at the bottom.

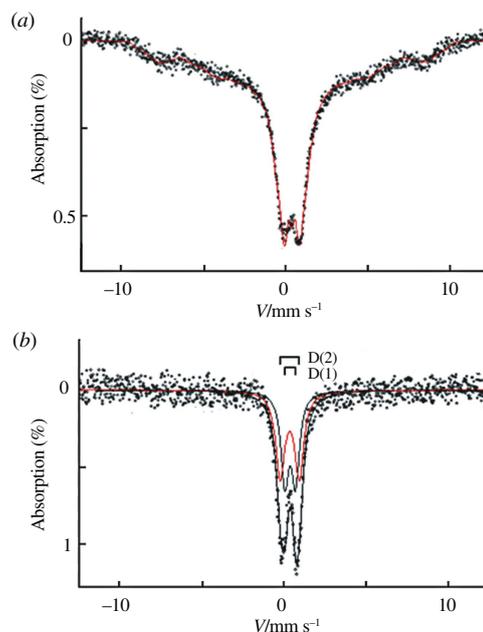


**Figure 1** Kinetics of MO decolorization in the presence of (1) antimony-monodoped  $x$  at%  $\text{Sb}^{5+}$ :  $\text{TiO}_2$ , (2) iron-monodoped  $x$  at%  $\text{Fe}^{3+}$ :  $\text{TiO}_2$ , and (3) codoped ( $x$  at%  $\text{Fe}^{3+}$  +  $x$  at%  $\text{Sb}^{5+}$ ):  $\text{TiO}_2$  powder samples.

of  $k_0$ . Therefore, the values of  $k_{(\text{Fe}+\text{Sb})}$  observed in the ( $\text{Fe}^{3+}$  +  $\text{Sb}^{5+}$ )-codoped samples showed that the presence of antimony diminishes the number of oxygen vacancies. Moreover, the suppression of oxygen vacancy formation was qualitatively confirmed by comparing the values of  $k_{(\text{Fe}+\text{Sb})}$  for the (0.6 at%  $\text{Fe}^{3+}$  + 0.6 at%  $\text{Sb}^{5+}$ ):  $\text{TiO}_2$  and (0.6 at%  $\text{Fe}^{3+}$  + 0.3 at%  $\text{Sb}^{5+}$ ):  $\text{TiO}_2$  samples (0.22 and 0.17  $\text{h}^{-1}$ , respectively). However, these results are inconsistent with a simple model for predicting the disappearance of  $\text{V}_\text{O}$  in samples containing equimolar amounts of  $\text{Fe}^{3+}$  and  $\text{Sb}^{5+}$ . The presence of residual oxygen vacancies means that the heterovalent cations  $\text{Fe}^{3+}$  and  $\text{Sb}^{5+}$ , besides their mutual charge compensation, preserve to some extent their own charge balances:  $2\text{Fe}^{3+} + \text{V}_\text{O}$  replace  $2\text{Ti}^{4+}$  and  $4\text{Sb}^{5+} + \text{V}_\text{Ti}$  replace  $5\text{Ti}^{4+}$ . Assuming that a change in the catalytic activity was caused by the annealing of residual  $\text{V}_\text{O}$  and  $\text{V}_\text{Ti}$  vacancies with the disappearance of  $\text{V}_\text{O}$ , we explained the observed decrease in the  $k_{(\text{Fe}+\text{Sb})}/k_{\text{Fe}}$  ratio (Figure 2) by a decrease in the rate of outward diffusion of  $\text{V}_\text{O}$  reflecting the formation of an increased number of  $\text{Fe}^{3+}-\text{V}_\text{O}$  associates.<sup>9</sup> Their presence was revealed by an analysis of the  $^{57}\text{Fe}$  Mössbauer spectrum of the 2 at%  $\text{Fe}^{3+}$ :  $\text{TiO}_2$  sample represented by a superposition of two quadrupole doublets having nearly equal spectral contributions. One of them, D(1), was assigned to the  $\text{Fe}^{3+}$  ion located on a site corresponding to its isomorphous substitution for  $\text{Ti}^{4+}$  (CN = 6), and the other, D(2), to the  $\text{Fe}^{3+}$  ion also located on an octahedral site but with one missing nearest neighbor  $\text{O}^{2-}$  (CN = 5). Therefore, it would be tempting to follow the evolution of the occupancies of these two sites in the studied series of ( $x$  at%  $\text{Fe}^{3+}$  +  $x$  at%  $\text{Sb}^{5+}$ ):  $\text{TiO}_2$  by determining a ratio between the areas of two doublets D(1) and D(2). Unfortunately, this cannot be done because of much lower concentrations of  $\text{Fe}^{3+}$  ions responsible



**Figure 2** Linear relation  $k_{(\text{Fe}+\text{Sb})}/k_{\text{Fe}} = -1.97x + 2.89$  between the ratio of the rate constants and the equimolar amount of Fe in ( $x$  at%  $\text{Fe}^{3+}$  +  $x$  at%  $\text{Sb}^{5+}$ ):  $\text{TiO}_2$  samples.



**Figure 3**  $^{57}\text{Fe}$  Mössbauer spectra of (a) the (0.6 at%  $\text{Fe}^{3+}$  + 0.6 at%  $\text{Sb}^{5+}$ ):  $\text{TiO}_2$  sample; (b) a magnetically less diluted 2 at%  $\text{Fe}^{3+}$ :  $\text{TiO}_2$  sample.

for drastic slowing down their electron spin relaxation, as revealed by the appearance of an unresolved magnetic hyperfine splitting pattern (Figure 3) prohibiting from any reliable assessment of quadrupole interactions related to different  $\text{Fe}^{3+}$  sites.

In conclusion, the observed evolution of photocatalytic activity upon equimolar co-doping with  $\text{Sb}^{5+}$  anyway has pointed to a significant residual effect of charge balance oxygen vacancies assumed to be involved in  $\text{Fe}^{3+}-\text{V}_\text{O}$  associates.

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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.2020.11.027.

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