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Mendeleev Commun., 2020, **30**, 383–384
Mendeleev Communications

Effect of charge balance vacancies on the ultraviolet photocatalytic activity of Fe^{3+}-doped anatase

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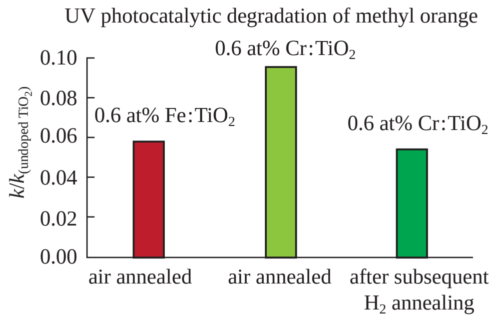
DOI: 10.1016/j.mencom.2020.05.041

The presence of Fe^{3+} dopant ions drastically decreases the activity of TiO_2 powders in the photocatalytic decolorization of methyl orange. A comparison of the photocatalytic activities of the 0.6 at% $Fe^{3+}:TiO_2$ and 0.6 at% $Cr^{3+}:TiO_2$ samples before and after their hydrogen annealing shows that this negative effect is mainly due to the formation of charge balance oxygen vacancies V_O, and it does almost not depend on the physicochemical properties of M^{3+} dopants. The ^{57}Fe Mössbauer spectrum of 2 at% $Fe^{3+}:TiO_2$ indicates that nearly every other Fe^{3+} ion introduced into TiO_2 possesses a vacancy V_O in its nearest surrounding.



Keywords: Fe^{3+}-doped TiO_2, photocatalytic activity, decolorization of methyl orange, charge balance vacancies, ^{57}Fe and ^{121}Sb Mössbauer spectra.

To increase the efficiency of solar energy conversion using TiO_2-based materials, they were often doped with heterovalent cations M^{n+} ($n \neq 4$).[1,2] Their presence in a large gap semiconductor, such as titanium dioxide, allows this material to absorb light with energy lower than the width of the gap ($E_g \approx 3$ eV). However, M^{n+}-doped photocatalysts can simultaneously lose their activity in both visible and UV light regions. Ikeda *et al.*[3] reported this effect for a reaction of oxygen evolution from an $AgNO_3$ solution in the presence of Cr^{3+}-doped rutile TiO_2 and suggested that the loss in photocatalytic activity was due to the formation of charge balance oxygen vacancies V_O and Cr^{6+} ions, both presumably playing the role of recombination centers toward photogenerated electrons (e^-) and holes (h^+). However, the individual effect of these lattice defects was not characterized. Recently, we succeeded to clarify this point by studying the kinetics of decolorization of methyl orange (MO) solutions under white light irradiation.[4] Photocatalytic activity of hydrogen annealed $Cr^{3+}:TiO_2$ samples (in the presence of V_O vacancies in surface layers) showed a drastic decrease, but it recovered to an initial level after air annealing (resulting in the regeneration of Cr^{6+}). Thus, we confirmed the expected role of V_O vacancies, whereas Cr^{6+} ions surprisingly appeared in this reaction as its active sites. Complementary information on charge-balancing defects can be obtained by comparing the kinetics of the above photocatalytic reaction studied under UV irradiation in the presence of TiO_2 doped with either Cr^{3+} or another M^{3+} cation. In contrast to the experiments performed under visible light, the ultraviolet photocatalytic activity (UVPA) no longer depends on the energy of impurity levels created by a M^{3+} ion, but it is determined by its charge-balancing defects. Accordingly, relevant information can be used for interpreting the photocatalytic data obtained under visible light.

In this work, we used Fe^{3+} as M^{3+} in order to reliably determine the valence state of iron and characterize its atomic surrounding using ^{57}Fe Mössbauer spectroscopy. All of the catalysts were single-phase anatase powders obtained using analytical grade chemicals by the annealing of $Ti(OH)_3$ co-precipitated with metal hydroxide dopant(s) in air at 500 °C for 2 h. To determine the virtual state of antimony in the co-doped $(Fe,Sb):TiO_2$ sample, we used ^{121}Sb Mössbauer spectroscopy. The doping solution of $Fe(NO_3)_3$ was enriched up to 10% in the ^{57}Fe isotope, while that of $SbCl_5$ was prepared using natural antimony. The ^{57}Fe Mössbauer spectra were recorded on a MS-1104 spectrometer at room temperature using a $^{57}Co(Rh)$ source; the isomer shift δ values are quoted relative to an α-Fe absorber. The ^{121}Sb Mössbauer spectra were recorded with a $Ca^{121m}SnO_3$ source at 100 K. To compare the photocatalytic activities we used the reaction rate constants of decolorization k. Before irradiation, which was carried out using a LED (λ = 370 nm, P = 3 W), a cuvette containing 5 mg of a catalyst and 1 ml of a MO solution was centrifuged to form a firm catalyst layer at the bottom. Optical density at λ = 460 nm was determined in the cuvette used for irradiation. Kinetic curves used to calculate k were approximated by a linear equation of first-order reactions.

We found that the UVPA of the 0.6 at% $Fe^{3+}:TiO_2$ sample was very low and close to that observed after the hydrogen annealing of an initially more active 0.6 at% $Cr^{3+}:TiO_2$ catalyst (Figure 1). This allowed us to suggest that, in the 0.6 at% $Fe^{3+}:TiO_2$ sample and the hydrogen annealed 0.6 at % $Cr^{3+}:TiO_2$ sample, the charge compensation was mainly implemented by V_O vacancies. This suggestion is consistent with a decrease in the UVPA observed in a series of Fe^{3+}-doped samples (x at% $Fe:TiO_2$) with increasing x and, consequently, with increasing number of V_O created by Fe^{3+} ions (Figure 2). Moreover, the same conclusion was made by

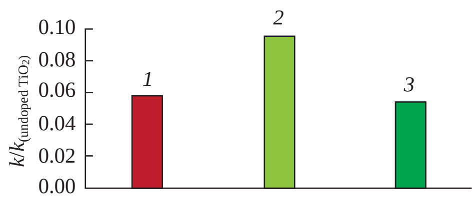


Figure 1 Kinetics of methyl orange decolorization in the presence of (*1*) 0.6 at% $Fe^{3+}:TiO_2$ and (*2*),(*3*) 0.6 at% $Cr^{3+}:TiO_2$ (*2*) before and (*3*) after its hydrogen annealing.

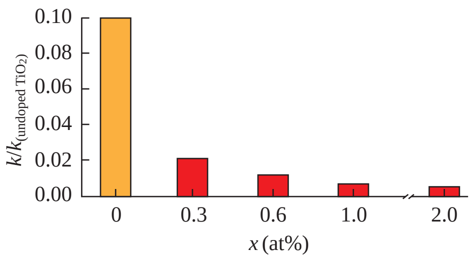


Figure 2 Dependence of the decolorization reaction rate constant k on the Fe^{3+} dopant concentration x in x at% $Fe^{3+}:TiO_2$.

fitting the ^{57}Fe Mössbauer spectrum of the 2 at% $Fe^{3+}:TiO_2$ sample (Figure 3) as a superposition of two symmetric doublets D(1) and D(2) characterized by the following parameters: (*a*) D(1), the isomer shift $\delta(1) = 0.35$ mm s^{-1}, the quadrupole splitting $\Delta E_Q(1) = 0.65$ mm s^{-1}, the full width at half maximum of each peak of the doublet $\Gamma(1) = 0.57$ mm s^{-1}, and the relative spectral contribution $A(1) = 47 \pm 5\%$; (*b*) D(2), $\delta(2) = 0.32$ mm s^{-1}, $\Delta E_Q(2) = 1.16$ mm s^{-1}, $\Gamma(2) = 0.67$ mm s^{-1}, and $A(2) = 53 \pm 5\%$.

The values of $\delta(1)$ and $\delta(2)$ imply a trivalent state of iron in the test catalyst. Thus, higher oxidation states of iron (characterized by negative values of δ) do not participate in the compensation of the Fe^{3+} charge deficit, unlike to that observed upon doping with Cr^{3+}. In this connection, note the absence of any spectral component ascribable to Fe^{2+} species (characterized by $\delta \geqslant 1.2$ mm s^{-1} and $\Delta E_Q \geqslant 2.2$ mm s^{-1}). Their creation being accompanied by an increase in the number of V_O might lead to an erroneous interpretation of the lower value of k observed in the presence of Fe-doped catalysts.

The most interesting feature of this ^{57}Fe Mössbauer spectrum is the occurrence of two doublets having close spectral contributions. Accordingly, the spectrum points to the location of ferric ions at two nonequivalent sites characterized by different electric field gradients acting on the Fe^{3+} nuclei. The Mössbauer parameters of D(1) are consistent with an isomorphous substitution of Fe^{3+} for Ti^{4+}. In this case, the Fe^{3+} ion is expected to find itself in a somewhat distorted octahedron [FeO_6], similar to those occurring in many ferric oxides characterized by ΔE_Q close to $\Delta E_Q(1)$. In contrast, the much higher value of $\Delta E_Q(2)$ is not typical of network-forming ferric ions. The value of $\Delta E_Q(2)$ is comparable with that of ΔE_Q assigned to a Fe^{3+} located on an octahedral site but with one missing O^{2-} neighbor ($\Delta E_Q = 1.06$ mm s^{-1}).[5] Hence, taking into account these earlier findings along with the observed spectral contributions of D(1) and D(2), the spectrum in Figure 3 allows us to infer the presence of a single V_O in the vicinity of nearly every other Fe^{3+} ion. Whereas it would perhaps be tempting to attribute D(2) to the surface-located Fe^{3+} ions, XPS measurements are required to verify this hypothesis. Note that a quite different catalytic effect was recently revealed in relevant oxides containing oxygen vacancies created at grain surfaces. The observed increase in the catalytic activity was presumably accounted for by an important role played by such vacancies in the formation of catalytically active species.[6] To get complementary information on the Fe^{3+} charge balance mechanism, we have investigated a co-doped sample (2 at% Fe^{3+} + 0.6 at% Sb^{5+})$:TiO_2$. In this case, the presence of Sb^{5+} *a priori* could partially suppress the formation of V_O and, consequently, increase both the value of k and the $A(1):A(2)$ ratio. However, our experiments have shown that the presence of antimony did not significantly affect the reaction kinetics and the occupancies of two iron sites. Note that the ^{121}Sb Mössbauer spectrum (Figure 4) exhibited the only peak characterized by $\delta \sim 0$ mm s^{-1}, which implies a pentavalent state of antimony. Thus, the incapability of this co-dopant to affect the UVPA of Fe^{3+}-doped TiO_2 could not be due to the partial reduction of Sb^{5+} to Sb^{3+} according to the 'auto compensation scheme', but it reflected an independent charge-balance mechanism of the Sb^{5+} dopant.[7] A similar effect was recently reported for the (2 at% Cr^{3+} + 0.6 at% Sb^{5+})$:TiO_2$ catalyst.[4]

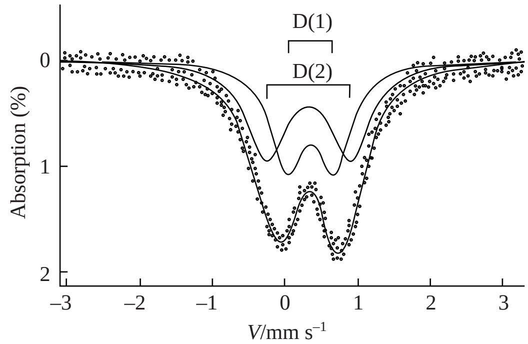


Figure 3 ^{57}Fe Mössbauer spectrum of the 2 at% $Fe:TiO_2$ sample.

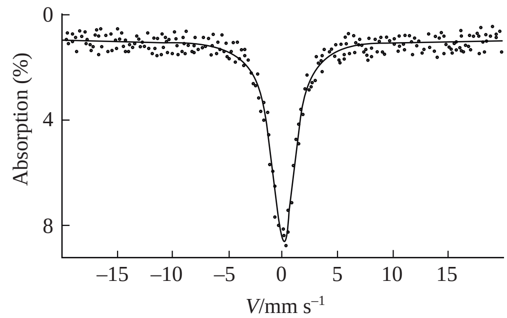


Figure 4 ^{121}Sb Mössbauer spectrum of the co-doped (2 at% Fe + + 0.6 at% Sb)$:TiO_2$ sample.

This work was supported by the Russian Foundation for Basic Research (grant no. 19-03-00061).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.05.041.

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Received: 27th November 2019; Com. 19/6070