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ScienceDirect
Mendeleev Commun., 2021, **31**, 896–898

Mendeleev
Communications

Effect of a long-term exposure of anatase TiO_2 powder doped with surface-located Sb^{3+} ions to UV radiation on its photocatalytic activity

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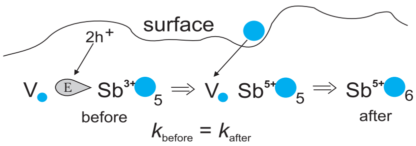
DOI: 10.1016/j.mencom.2021.11.043

Ultraviolet photocatalytic experiments on the kinetics of decolorization of methyl orange and the ^{121}Sb Mössbauer characterization of the title catalyst were performed. The stereochemically active electronic lone pair of Sb^{3+} was found to completely deactivate the neighboring oxygen vacancy as a recombination center towards the photogenerated electrons and holes.

Oxidation of Sb^{3+} does not affect the kinetics of the methyl orange decolorization



Keywords: Sb-doped TiO_2, photocatalytic decolorization, methyl orange, ^{121}Sb Mössbauer spectroscopy, Sb^{3+} electronic lone pair, stereochemical activity.

Earlier, we have demonstrated[1] the possibility to stabilize tin dopant ions at uppermost surface layers of anatase TiO_2 crystallites and were the first to investigate physicochemical processes occurring at the $Ti_{1-x}Sn_xO_2$/gas interface using ^{119}Sn Mössbauer spectroscopy. The test samples were synthesized by the hydrogen annealing of $Ti_{1-x}Sn_xO_2$ powder obtained by calcination of co-precipitated Ti^{IV} and Sn^{IV} hydroxides in air. In the course of hydrogen annealing, surface Sn^{4+} ions were reduced to a divalent state and located on low coordination sites (CN < 6), which are energetically unfavorable for Ti^{4+}, owing to their stereochemically active electronic lone pair E. A similar behavior was observed for isoelectronic Sb^{3+} dopant ions, also possessing both the lone pair E and the Mössbauer isotope ^{121}Sb, which were also located at surface sites of anatase upon hydrogen annealing.[2] However, this technique was not used previously to study the modifying effect of surface dopant cations on the photocatalytic activity of this oxide, the main component of promising materials for solar energy conversion.[3–5] Therefore, we investigated the activity of TiO_2-based samples in the ultraviolet photocatalytic decolorization of methyl orange (MO) to clarify the modifying action of bulk Fe^{3+} ions using ^{57}Fe Mössbauer spectroscopy.[6] The introduction of 0.6 at% Fe^{3+} resulted in a decrease in the reaction rate constant by a factor of about 8. A similar effect reported[7] for another photocatalytic reaction was explained by the formation of charge-compensating oxygen vacancies V_O playing the role of (e^-,h^+)-recombination centers towards photogenerated electrons e^- and holes h^+ in the structure of TiO_2. Surprisingly, a much feeble slowing down was observed[8] in the reaction of MO decolorization in the presence of 0.5 at% Sb^{3+}. These trivalent ions were located on surface sites with CN < 6 allowing the Sb^{3+} lone pair E to exhibit its stereochemical activity.[9] Thus, we suggested that the hybridization of 5*s* and 5*p* orbitals, which resulted in moving the negative charge density of E towards the neighboring V_O, can weaken the undesirable impact of the latter. We performed photocatalytic experiments in order to determine the rate constant of decolorization in the presence of TiO_2 containing $^{UV}Sb^{5+}$ daughter ions. These ions resulted from the oxidation of parent surface-located Sb^{3+} ones by the photogenerated holes upon a sufficiently long-term exposure of Sb^{3+}/TiO_2 powder to UV radiation.[2] For this purpose, anatase powder, which was prepared by the annealing of precipitated $Ti(OH)_4$ in air at 500 °C for 2 h, was wetted with an ammonia solution and then impregnated with a solution of $SbCl_5$ to obtain a precursor containing 0.6 at% Sb^{5+}. Rapid hydrolysis of $SbCl_5$ upon contact with ammonia led to the formation of a $Sb(OH)_5$ shell around the impregnated grains. After washing the powder with deionized water, it was first annealed in air at 400 °C for 1 h and then in hydrogen at 300 °C for 2 h. The X-ray diffraction patterns of the test materials revealed the presence of single-phase anatase TiO_2 (space group $I4_1/amd$). The reduction of the pristine Sb^{5+} ions to a trivalent state was assessed using Mössbauer spectroscopy. The surface location of antimony in materials obtained by the same synthesis procedure was confirmed earlier[2] by XPS: a 3–5 nm thick surface adjacent layer was enriched in antimony by a factor of 6, as compared with the nominal Sb concentration in the material as a whole ([Sb] : [Ti] = 0.006). Preliminary ^{121}Sb Mössbauer measurements showed that trivalent antimony did not undergo oxidation under ambient air for at least a one-month storage period.

In this work, the UV exposure duration was 220 h. A Wood's lamp (λ = 370 nm, P = 25 W) was used to irradiate hydrogen-annealed Sb^{3+}/TiO_2. Prior to exposure, ~750 mg of Sb^{3+}/TiO_2 powder and 5 cm^3 of deionized water were introduced into a thin-walled glass test tube (water was used as a scavenger of electrons generated within TiO_2 upon UV irradiation). Another part of Sb^{3+}/TiO_2 powder was also introduced along with 5 cm^3 of H_2O into a similar test tube, which was placed in the dark. After 220 h, both of the tubes were heated at 90 °C for 2 h. The irradiated material (sample **1**) and the nonirradiated reference sample (**2**) were used in Mössbauer measurements and ultraviolet photocatalytic experiments.

The ^{121}Sb spectra were recorded on a MS-1104 spectrometer and analyzed by a least-square fitting program. The 8.5 keV escape peak produced by Mössbauer gamma rays (E_γ = 37.15 keV) in a thin NaI(Tl) scintillator was used to perform resonant absorption measurements with antimony-121. In these measurements, both the source $Ca^{121m}SnO_3$ and the test sample (absorber) were introduced into the hole of a copper bar immersed in a Dewar flask filled with liquid nitrogen. Under these conditions, the temperature of both the source and the absorber was close to 100 K.

A LED (λ = 370 nm, P = 3 W) was used in the photocatalytic experiments. Optical density was determined at λ = 460 nm in the cuvette used for irradiation. To compare the photocatalytic activities, we used the reaction rate constants k of MO decolorization, which were calculated using a linear equation of first-order reactions.

The ^{121}Sb Mössbauer spectrum of the pristine hydrogen-annealed sample Sb^{3+}/TiO_2 [Figure 1(*a*)] contained two resonant absorption peaks. A peak at negative Doppler velocity values was represented by an unresolved pattern of quadruple splitting whose spectral parameters (Table 1) are typical of the Sb^{3+} ion possessing a stereochemically active pair E in an oxide compound.[10–12] The parameters of the other less intense narrow peak in the central part of the spectrum are typical of the Sb^{5+} ion on a site octahedrally coordinated by O^{2-} ions.[10–12] These residual unreduced Sb^{5+} cations can be assigned to those penetrated in deeper surface layers upon preliminary annealing in air at 400 °C. Thus, this spectrum indicated the reduction of the majority of Sb^{5+} ions to a trivalent state upon the hydrogen annealing. Note that, according to Figure 1(*a*), no metallic Sb^0 (expected to be characterized by a narrow peak at $v \sim -11.6$ mm /s [11]) was formed due to an increased stability of surface-located Sb^{3+} ions, as compared to that in amorphous $Sb(OH)_3$ precipitates after a similar reducing treatment. As can be seen in Figure 1(*b*), the UV irradiation of the pristine sample resulted in a considerable increase in the spectral contribution of Sb^{5+} at the expense of Sb^{3+}. This spectrum evidenced the reoxidation of Sb^{3+} (sample **1**) with a decrease in the number of vacancies V_O presumably affected by the neighboring E. By contrast, the spectrum of **2** [Figure 1(*c*)] exhibited no significant changes. Therefore, it can be surprising that the oxidation of Sb^{3+}, which was revealed by the Mössbauer spectrum [see Figure 1(*b*)], in the subsequent photocatalytic experiments (see Table 1) did not affect the value of k_1 characterizing **1**. Nevertheless, the oxidation of Sb^{3+} by holes obviously implies the suppression of the effect of the neighboring E; consequently, it should enhance the negative photocatalytic impact of the relevant V_O in contrast to experimentally observed facts. Therefore, it should be taken into account that oxygen vacancies were no more needed for the Sb^{5+} charge balance, allowing one to expect their annealing upon outward diffusion resulting in the increase in the photocatalytic activity. Accordingly, the value of k_1 is anticipated to overcome that of k_2 (reference material **2**) due to a higher efficiency of normal vacancy V_O as a (e^-,h^+)-recombination center, as compared with that affected by E. Hence, the equality $k_1 = k_2$ actually signifies that E completely deactivated the relevant V_O. However, the slowed down kinetics observed in the presence of either **1** or **2,** as compared with that in the presence of undoped TiO_2, should be clarified. This can be due to the presence, in deeper surface layers of both antimony-doped catalysts, of significant amounts of Sb^{5+} ions (~0.1 at% according to the ^{121}Sb Mössbauer spectra). Their charge balance mechanism may consequently involve the formation of Ti^{4+} vacancies (V_{Ti}) according to the scheme $4Sb^{5+} + V_{Ti}$ substitute for $5Ti^{4+}$, the titanium vacancy formed being capable of playing the role of (e^-,h^+)-recombination centers as it was the case of V_O.

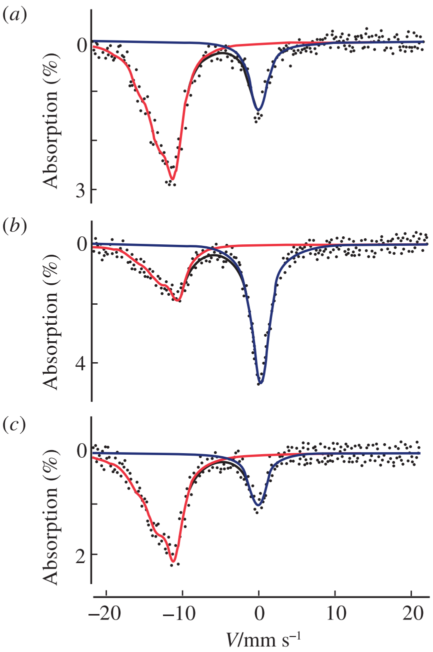


Figure 1 ^{121}Sb Mössbauer spectra of (*a*) the pristine hydrogen-annealed 0.6 at% Sb/TiO_2 sample, (*b*) the UV-irradiated sample **1,** and (*c*) the unirradiated reference sample **2**.

Table 1 Mössbauer spectroscopic parameters of Sb/TiO_2 samples and the reaction rate constant ratios k/k_0 of the ultraviolet photocatalytic decolorization of MO.[a]

Materials and k/k_0 ratios	Spectral components	δ/mm s^{-1}	$eV_{zz}Q_{5/2}$/ mm s^{-1}	Γ/ mm s^{-1}	A (%)
Sb/TiO_2 (pristine)	Sb^{3+}	–12.2 ± 0.2	17.7 ± 1.2	2.7 ± 0.2	77 ± 5
k/k_0 = 0.57 ± 0.09	Sb^{5+}	0.04 ± 0.09	1.5 ± 1.4	2.5 ± 0.2	23 ± 5
1 (UV-irradiated)	Sb^{3+}	–12.0 ± 0.2	19.4 ± 1.5	2.7 ± 0.2	39 ± 5
k_1/k_0 = 0.44 ± 0.06	Sb^{5+}	0.31 ± 0.04	2.3 ± 1.9	2.7 ± 0.2	61 ± 5
2 (unirradiated	Sb^{3+}	–12.3 ± 0.2	18.5 ± 1.4	2.7 ± 0.2	**78** ± 5
reference) k_2/k_0 = 0.43 ± 0.06	Sb^{5+}	0.21 ± 0.09	3.0 ± 2.8	2.5 ± 0.2	22 ± 5

[a] δ is the isomer shift relative to the $Ca^{121m}SnO_3$ source; $eV_{zz}Q_{5/2}$ is the quadrupole coupling constant of the ^{121}Sb ground state; Γ is the full width at half maximum of each peak; A is the spectral contribution; and k/k_0 is a ratio between the reaction rate constants in the presence of the test material and undoped TiO_2, respectively.

In conclusion, this ^{121}Sb Mössbauer spectroscopic study devoted to a comparison of the reaction rate constants of the photocatalytic decolorization of MO in the presence of 0.6 at% Sb/TiO_2 samples has revealed a strong deactivating effect of the lone pair of Sb^{3+} on the efficiency of the neighboring V_O as a (e^-,h^+)-recombination center.

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.2021.11.043.

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Received: 31st May 2021; Com. 21/6572