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Application of the ^{121}Sb Mössbauer spectroscopy to characterizing titania-based photocatalysts modified by lone pair cations

Mikhail V. Korolenko, Pavel B. Fabritchnyi* and Mikhail I. Afanasov

Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation.
Fax: +7 495 932 8846; e-mail: pf@radio.chem.msu.ru

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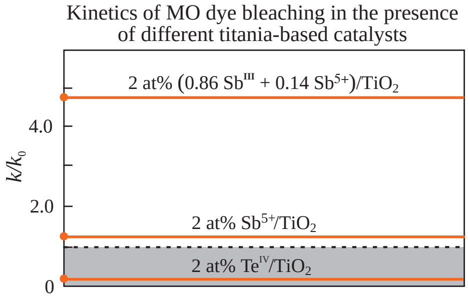
A study of the reaction of white light photocatalytic bleaching of methyl orange solutions in the presence of antimony-modified anatase TiO_2 catalysts has revealed a nearly 5-fold increase in the reaction rate constant k in comparison with k_0 for the undoped reference TiO_2. Analysis of ^{121}Sb spectra has shown that this effect is due to the stereoactive electronic lone pair E of Sb^{III} species. Our experiments have thus confirmed the mechanism of its positive modifying action theoretically predicted earlier for the isoelectronic lone pair dopant Sn^{II}.


Kinetics of MO dye bleaching in the presence of different titania-based catalysts

Keywords: Sb^{III}-doped anatase TiO_2, ^{121}Sb Mössbauer spectra, visible light photocatalytic activity, Sb^{III} electronic lone pair, photocatalytic bleaching.

Over the past decade, the growing interest in experimental methods of assessing the photocatalytic activity of titania doped by elements such as tin, antimony or tellurium[1–6] was largely due to the application of the density functional theory (DFT) simulations to explore the effect of their stereochemically active electronic lone pair E. The authors[7] have concluded that $(SnO)_n$ nanoclusters supported on the anatase α-TiO_2 (*001*) surface allow one to successfully overcome two main obstacles limiting the efficiency of the mentioned large-gap semiconductor (E_g = 3.2 eV). It was therefore anticipated that the interaction of an E Sn^{II} atom with the surface could both create new energy levels narrowing the gap and, most importantly, enhance charge separation of photogenerated charges. Electrons (e^-) thus appeared to be associated with surface-located Ti^{4+} ions while holes (h^+) retained at E Sn^{II}, thereby hampering electron-hole recombination. However, the experimental verification of those theoretical predictions was found not to be an easy task. For instance, ^{119}Sn Mössbauer spectra of E Sn^{II} atoms located upon hydrogen annealing, on α-TiO_2 crystallite surfaces have revealed[8] rapid oxidation of Sn^{II} to the tetravalent state upon subsequent contacting ambient air. The observed oxidation hence made impossible any direct assessment of the effect of E Sn^{II} on the photocatalytic activity. We consequently attempted to use for this purpose the isoelectronic atoms Sb^{III}, which possess both the stereochemically active lone pair E and Mössbauer isotope ^{121}Sb, but at the same time are resistant to oxidation by ambient air.

To synthesize the antimony-doped polycrystalline α-TiO_2 samples we used a procedure similar to the reported by the authors[9] who, to our knowledge, were the first to investigate the visible-light photocatalytic activity of the Sb^{5+}-doped α-TiO_2. Their procedure involved the use of a precursor obtained by adding NH_4OH to a mixture of appropriate volumes of $TiCl_4$ and $SbCl_5$ solutions. The final annealing of the co-precipitated hydroxide precursor was carried out in air at 500 °C for 2 h. It was established[9] that doping with Sb^{5+} resulted in a significant increase in the photocatalytic activity.[†] The procedure we have used in the present work was however somewhat modified. First, upon the co-precipitation of hydroxides a solution of $SbCl_3$ instead of $SbCl_5$ was used and, second, annealing of the precursor was performed under argon atmosphere. As a test reaction we again used the photocatalytic bleaching of the aqueous solutions of methyl orange (MO). All the photocatalysts studied in this work were found to be single-phase anatase α-TiO_2 (space group $I4_1/amd$). ^{121}Sb Mössbauer spectra were recorded at 100 K using a $Ca^{121m}SnO_3$ source. Subsequent visible-light photocatalytic experiments were carried out using an appropriate LED (white light, color temperature T_c = 6500 K, P = 3W). Optical density was determined at λ = 460 nm in the cuvette applied for irradiation. To compare the photocatalytic activities, the rate constants k were calculated using a kinetic equation of first-order reactions.

It is known[10] that the valence state of antimony in its various oxides can be reliably identified by ^{121}Sb Mössbauer spectroscopy, while it was not the case with X-ray photoelectron spectroscopy previously applied[4] to studying the photocatalytic properties of Sb-doped rutile TiO_2. The advantage of the former spectroscopic method is due to a relatively large change in the ^{121}Sb nucleus radius R upon emission of the resonant γ ray ($\Delta R/R = -8.8 \times 10^{-4}$).[11] This results in the increased dependence of the observed isomer shift δ value on that of the total electron density $|\Psi(0)|^2$ at ^{121}Sb nucleus, which allows one to determine the valence state of the antimony atom concerned. Moreover, the ^{121}Sb quadrupole hyperfine coupling able to significantly distort the shape of the observed Mössbauer spectrum permits to assess the value of the electric field gradient eV_{zz}, probed by the resonant nucleus and, consequently, reveal the presence of the lone pair E.

[†] This finding thus suggests that in the studied catalysts the charge compensation of the Sb^{5+} excessive charge should involve, as it was the case in a Sb^{5+}-doped rutile TiO_2[4], the formation of cationic vacancies $V_{Ti^{4+}}$ allowing the antimony-doped titania to preserve its pristine insulating behavior.

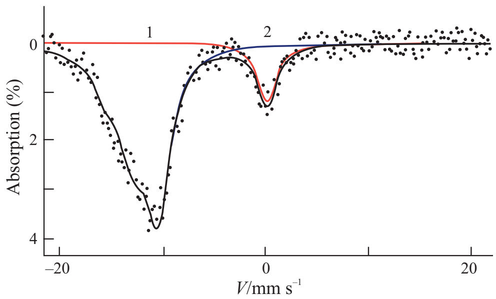


Figure 1 ^{121}Sb Mössbauer spectrum of catalyst 2 at% $\mathrm{Sb^{III}}{\downarrow}/\alpha\text{-}\mathrm{TiO_2}$ recorded at 100 K.

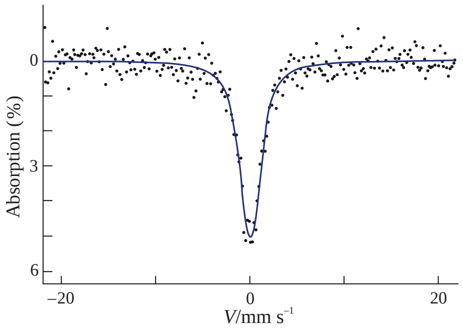


Figure 2 ^{121}Sb Mössbauer spectrum of catalyst 2 at% $\mathrm{Sb^{5+}}/\alpha\text{-}\mathrm{TiO_2}$ recorded at 100 K.

^{121}Sb Mössbauer spectrum of the sample modified by co-precipitation of 2 at% $\mathrm{Sb^{III}}$ (catalyst 2% $\mathrm{Sb^{III}}{\downarrow}/\mathrm{TiO_2}$) is shown in Figure 1. It clearly displays the presence of two distinct maxima of resonant absorption, corresponding to different valence states of antimony, the relevant absorption peaks being hereafter denoted as spectral components 1 and 2. The values of the hyperfine parameters related to the dominant component 1 (the spectral contribution $A_1 \geqslant 86\%$, $\delta_1 = -11.7 \pm 0.3$ mm s^{-1} and the quadrupole coupling constant $[eV_{zz}Q_{5/2}]_1 = 18.9 \pm 1.5$ mm s^{-1}) are close to the reported earlier for $\mathrm{Sb^{III}}$ located at the surfaces of α-TiO$_2$ crystallites.[12‡] The relevant values related to the minor component 2 ($A_2 \leqslant 14\%$, $\delta_2 = 0.20 \pm 0.15$ mm s^{-1}, $[eV_{zz}Q_{5/2}]_2 = 2.8 \pm 0.9$ mm s^{-1}) allow ascribing it to $\mathrm{Sb^{5+}}$ located in distorted octahedral $[\mathrm{SbO_6}]$ groups.[13] Their appearance could be indicative of partial auto-compensation of charges of the heterovalent antimony dopants occurring in some of TiO$_2$ crystallites. Despite the mixed valence state of antimony in the catalyst 2% $\mathrm{Sb^{III}}{\downarrow}/\mathrm{TiO_2}$, as it was revealed by its Mössbauer spectrum, the much weaker contribution of component 2 could not lead to a significant error upon assessing the photocatalytic impact of the $\mathrm{Sb^{III}}$ species, which represent the large majority of the antimony atoms in the considered catalyst.

Our photocatalytic experiments performed with catalyst 2 at% $\mathrm{Sb^{III}}{\downarrow}/\mathrm{TiO_2}$ have shown that presence of $\mathrm{Sb^{III}}$ has drastically increased the value of the rate constant $k_{(2\%\ \mathrm{Sb^{III}}\downarrow/\alpha\text{-}\mathrm{TiO_2})}$ as compared with that (k_0) for the annealed in argon undoped reference α-TiO$_2$ ($k_{(2\%\ \mathrm{Sb^{III}}\downarrow/\alpha\text{-}\mathrm{TiO_2})}/k_0 = 4.6 \pm 0.4$).[§]

Thus, this experimental finding is consistent with the earlier predicted[7] positive effect of the electronic lone pair on the visible light photocatalytic efficiency of α-TiO$_2$. Nevertheless, to corroborate this conclusion, we have also assessed the activity of catalyst 2 at% $\mathrm{Sb^{5+}}/\alpha\text{-}\mathrm{TiO_2}$ which was obtained by annealing the precursor co-precipitated from a solution containing $\mathrm{Sb^{5+}}$ ions exempt from lone pair E. The ^{121}Sb Mössbauer spectrum of this catalyst allowed us to ascertain that antimony atoms have retained their pristine pentavalent state (Figure 2). Similar photocatalytic measurements performed in the presence of 2 at% $\mathrm{Sb^{5+}}/\alpha\text{-}\mathrm{TiO_2}$ have evidenced a several times smaller increase in the reaction rate constant ($k_{(2\%\ \mathrm{Sb^{5+}}/\alpha\text{-}\mathrm{TiO_2})}/k_0 = 1.18$) as compared with the observed in the previous case. Hence, this experiment has definitively proved that the drastic increase in the activity of catalyst 2 at% $\mathrm{Sb^{III}}{\downarrow}/\mathrm{TiO_2}$ is due to the lone pair E $\mathrm{Sb^{III}}$.

Taking into account the results obtained for the catalyst doped with E $\mathrm{Sb^{III}}$, it would be very tempting to get insight on the photocatalytic effect of isoelectronic dopant atoms E $\mathrm{Te^{IV}}$ known to be more resistant to oxidation than the E $\mathrm{Sb^{III}}$ ones. Accordingly, we have prepared the relevant sample 2 at% $\mathrm{Te^{IV}}{\downarrow}/\mathrm{TiO_2}$ and studied the kinetics of the same test reaction. The measurements performed have rather unexpectedly shown the doping with 2 at% $\mathrm{Te^{IV}}$ to result in a drastic decrease in the activity of the catalyst concerned ($k_{(2\%\ \mathrm{Te^{IV}}/\alpha\text{-}\mathrm{TiO_2})}/k_0 = 0.1$). This finding could be related to the high chemical inertness of $\mathrm{Te^{IV}}$ species which prohibits them from further oxidation and, obviously, does not favor separating the photogenerated holes at $\mathrm{Te^{IV}}$ electronic lone pairs.

In conclusion, this study has demonstrated that the ^{121}Sb Mössbauer spectroscopic probe can be successfully used upon developing other antimony-doped oxide materials.

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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.2023.10.042.

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[‡] XPS measurements[12] have revealed an abnormally high (more than 6 times larger) enrichment with antimony of thin surface-adjacent layers compared with the overall molar ratio antimony-to-titanium defined by the amounts of antimony and titanium used in the synthesis of the relevant sample.

[§] The catalyst 2% $\mathrm{Sb^{III}}{\downarrow}/\mathrm{TiO_2}$ used in this experiment was then again tested in bleaching the same volume of fresh MO solution in order to compare the values of the rate constant k determined in two successive measurements. No significant difference was observed between the obtained values of $k_{(2\%\ \mathrm{Sb^{III}})}/k_0$. Thus, upon this supplementary bleaching 2% $\mathrm{Sb^{III}}{\downarrow}/\mathrm{TiO_2}$ was found to retain its initial photocatalytic efficiency.