## LETTERS TO THE EDITOR

# Effect of Protonation on the Photocatalytic Activity of the Layered Titanate Rb<sub>2</sub>Nd<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub>

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**Abstract**—It was found that the contact of the layered oxide  $Rb_2Nd_2Ti_3O_{10}$  with an aqueous solution gives rise to a protonation process, which leads to lowering the oxide photocatalytic activity in reactions of hydrogen evolution from a water-alcohol solution.

Keywords: layered oxide, titanate, hydration, protonation, photocatalysis, hydrogen

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Layered perovskite-like titanates  $A_2Ln_2Ti_3O_{10}$  (A being alkaline metal, Ln being lanthanide) related to Ruddlesden–Popper phases are promising photocatalysts [1]. Their high photocatalytic activity in water decomposition is often referred to the possibility of intercalating water molecules into the interlayer space, which is considered as a reaction zone along with the crystal surface [2, 3]. When the cation radius of the alkali metal A in the composition of  $A_2Ln_2Ti_3O_{10}$  titanates increases, their ability to water intercalation and simultaneously the photocatalytic activity increase [4]. In this regard, Rb-containing phases are of particular interest for the study.

We have found that the layered titanate  $Rb_2Nd_2Ti_3O_{10}$ on contact with aqueous solution is not only subjected to the intercalation of water in the interlayer space, but also to protonation, i.e. to the substitution of protons for the interlayer rubidium cations. As a result a number of hydrated-protonated phases with the common formula  $H_x Rb_{2-x} Nd_2 Ti_3 O_{10} \cdot y H_2 O$  are formed, each being stable within a certain range of solution acidity. In this case amount of intercalated water (y) decreases in the series of these phases as the protonation degree (x) increases, which can affect their photocatalytic properties. The aim of this work was to study photocatalytic activity of the new layered titanate Rb<sub>2</sub>Nd<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub> and its dependence on intercalation and ion exchange processes occurring on the contact of the layered oxide with aqueous solutions.

Layered titanate  $Rb_2Nd_2Ti_3O_{10}$  was synthesized by the ceramic technique from the corresponding simple oxides and carbonates  $TiO_2$  ( $\geq$ 99.9%),  $Nd_2O_3$  ( $\geq$ 99.9%), and  $Rb_2CO_3$  ( $\geq$ 99.8%). The reagents were taken in stoichiometric ratios in accordance with reaction (1):

$$Rb_2CO_3 + Nd_2O_3 + 3TiO_2 = Rb_2Nd_2Ti_3O_{10} + CO_2\uparrow.$$
 (1)

Rubidium carbonate was taken in excess of 40% to compensate for its losses due to evaporation at high temperature. The charge was ground in an agate mortar, pressed into tablets, and calcined in air according to the temperature program 700°C, 6 h + 1000°C, 10 h. To obtain three stable hydrated-protonated forms of the compositions HRbNd<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub>·0.8H<sub>2</sub>O, H<sub>1.5</sub>Rb<sub>0.5</sub>Nd<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub>·0.6H<sub>2</sub>O, and H<sub>2</sub>Nd<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub>·0.4H<sub>2</sub>O, weighted quantities of 0.3 g of initial samples were added to 50 mL of distilled water and aqueous solutions of hydrochloric acid with concentrations of 0.016 and 0.1 M, respectively. The resulting suspensions were stirred for 24 h and then the precipitates were separated by centrifugation.

The phase composition was controlled at each stage of the synthesis by the X-ray phase analysis (Rigaku Miniflex II,  $CuK_{\alpha}$ ). The hydration and protonation degrees were confirmed by the thermogravimetric method (TG 209 F1 Libra, Netzsch) and energydispersive X-ray microanalysis (Oxford Instruments INCAx-act). The band gap energy was determined by the diffuse reflection spectroscopy (Shimadzu UV-

2550, ISR-2200) using Kubelka-Munk transformation. Photocatalytic activity was studied in the model reaction of hydrogen evolution from ethyl alcohol aqueous solution with a mole fraction of 1%. Simultaneously with hydrogen evolution ethanol is oxidized in such a system to acetaldehyde in the stoichiometric amount. The photocatalytic experimental technique is described in detail in [4]. The irradiation was carried out with a DRT-125 UV lamp using a liquid light filter cutting off radiation with wave lengths less than 220 nm. The amount of evolved hydrogen was determined by gas chromatography (Shimadzu GC-2014 with a system of online sampling, thermal conductivity detector, carrier gas argon). Volume of the reaction suspension was 50 mL, photocatalyst content in the suspension 1 mg/mL.

The maximal rate of hydrogen evolution of 8.7  $\mu$ mol/h was observed for the sample HRbNd<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub>· 0.8H<sub>2</sub>O. It should be noted that this metastable form of the layered oxide has the lowest protonation degree and is almost immediately formed on contact of initial Rb<sub>2</sub>Nd<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub> with distilled water. However more substituted samples H<sub>1.5</sub>Rb<sub>0.5</sub>Nd<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub>·0.6H<sub>2</sub>O and H<sub>2</sub>Nd<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub>·0.4H<sub>2</sub>O showed significantly lower photocatalytic activity of 1.4  $\mu$ mol/h and 1.0  $\mu$ mol/h, respectively. The rate of hydrogen evolution for the P25 Evonik-Degussa commercial photocatalyst TiO<sub>2</sub> in similar conditions was 3.5  $\mu$ mol/h.

On the one hand, the observed trend is correlated with a decrease in the amount of sorbed water with increasing protonation degree and thus is an indirect evidence in favor of the fact that intercalated water plays an important role in the photocatalytic process, being oxidized in the interlayer space. On the other hand, as the protonation degree increases, a slight decrease in the band gap from 3.60 eV for HRbNd<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub>·0.8H<sub>2</sub>O to 3.54 eV for H<sub>2</sub>Nd<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub>· 0.4H<sub>2</sub>O is also observed. As in the range of 3.54– 3.60 eV there are no radiation bands of the lamp in use, we can conclude that this change has no effect on the number of absorbed photons. However, it should lower the reactivity of photogenerated electrons and holes owing to a displacement of edges of conduction and valence bands. This also may contribute to the observed decrease in the photocatalytic activity.

Thus, the substitution of protons for rubidium cations in the interlayer space of layered oxide  $Rb_2Nd_2Ti_3O_{10}$  leads to lowering its photocatalytic activity, therefore it is advisable to use this oxide as a photocatalyst only in alkaline media, where the protonation occurs to a lesser extent.

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