

# Comparison of $\text{NaNbO}_3$ AND $\text{NaTaO}_3$ as the photocatalysts in the reaction of hydrogen generation

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The photocatalytic production of hydrogen over several chemical compounds based on sodium niobates and tantalates has been investigated. The photocatalysts have been prepared by an impregnation method of  $\text{Nb}_2\text{O}_5$  and  $\text{Ta}_2\text{O}_5$  in the aqueous solution of sodium hydroxide and then the calcination at the temperature range of 450 – 800°C. In this report, we present the study showing that of the catalysts explored, the highest photocatalytic activity was shown in a sample obtained at the temperature of 450°C and containing  $\text{NaTaO}_3$  as a main phase.

**Keywords:**  $\text{NaNbO}_3$ ,  $\text{NaTaO}_3$ , photocatalysis, hydrogen generation.

## INTRODUCTION

Recently, many studies have been performed to develop heterogeneous photocatalysis for water splitting into hydrogen and oxygen<sup>1–3</sup>. However, the number of photocatalytic materials found is still limited and the active materials being employed are mainly  $\text{TiO}_2$  and titanates. Moreover, the efficiency of photocatalytic hydrogen evolution is relatively low and many photocatalysts will deactivate after a long-term irradiation. Therefore, a development of highly efficient photocatalysts becomes a hot topic in the field of photocatalysis.

$\text{NaNbO}_3$  and  $\text{NaTaO}_3$  are well-known perovskite oxides ( $\text{ABO}_3$ ) which possess attractive physical properties such as low density, high sound velocity and are useful for ferroelectric and piezoelectric applications<sup>4</sup>. On the other hand, both of those materials can be candidates as photocatalysts for the reaction of photocatalytic hydrogen generation. Traditionally,  $\text{NaNbO}_3$  and  $\text{NaTaO}_3$  have been synthesized via solid state reaction of alkali metal carbonates and  $\text{Nb}_2\text{O}_5/\text{Ta}_2\text{O}_5$  and the temperature of 800°C or above, which sometimes leads to inhomogeneity in composition and coarse particles. Additionally, the problem with preparing alkaline niobates and tantalates is that high temperatures of calcination can lead to the volatilization of alkaline species, resulting in the formation of undesirable secondary phases<sup>4–5</sup>.

In the current study, the efficiency of  $\text{NaNbO}_3$  and  $\text{NaTaO}_3$  used as catalysts in the photocatalytic hydrogen generation will be presented. The photocatalytic reactions were carried out in the presence of formic acid as an electron donor.

## EXPERIMENTAL

High purity grade niobium pentoxide, tantalum pentoxide ( $\text{Nb}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$ , purity 99.99%) and sodium hydroxide ( $\text{NaOH}$ ) supplied by Sigma-Aldrich were used as precursors for the synthesis of sodium niobate and tantalate ( $\text{NaNbO}_3$ ,  $\text{NaTaO}_3$ ). In the first step of the photocatalyst preparation,  $\text{Nb}_2\text{O}_5$  or  $\text{Ta}_2\text{O}_5$  were impregnated in the aqueous solution of sodium hydroxide. The molar ratio of  $\text{Na}/\text{Nb}_2\text{O}_5$  and  $\text{Na}/\text{Ta}_2\text{O}_5$  was 2:1. After impregnation, the obtained materials were dried at the temperature of 110°C for 24 hours. The dried materials were

divided into seven equal parts and each of them was calcinated with a certain temperature from the range of between 450 – 800°C with the step of 50°C. The calcination step at the required temperature was fixed for 11 hours. During the catalysts preparation procedure some amount of  $\text{NaOH}$  evaporated and in order to keep its concentration at the constant level the additional portion of  $\text{NaOH}$  solution was introduced into the sample. The excess of the alkali in the samples was washed out with distilled water. The photocatalysts prepared in the above-mentioned way are labeled in the following manner:  $\text{Na}/\text{Nb}_2\text{O}_5\text{-T}$  and  $\text{Na}/\text{Ta}_2\text{O}_5\text{-T}$  (T means the temperature of calcination).

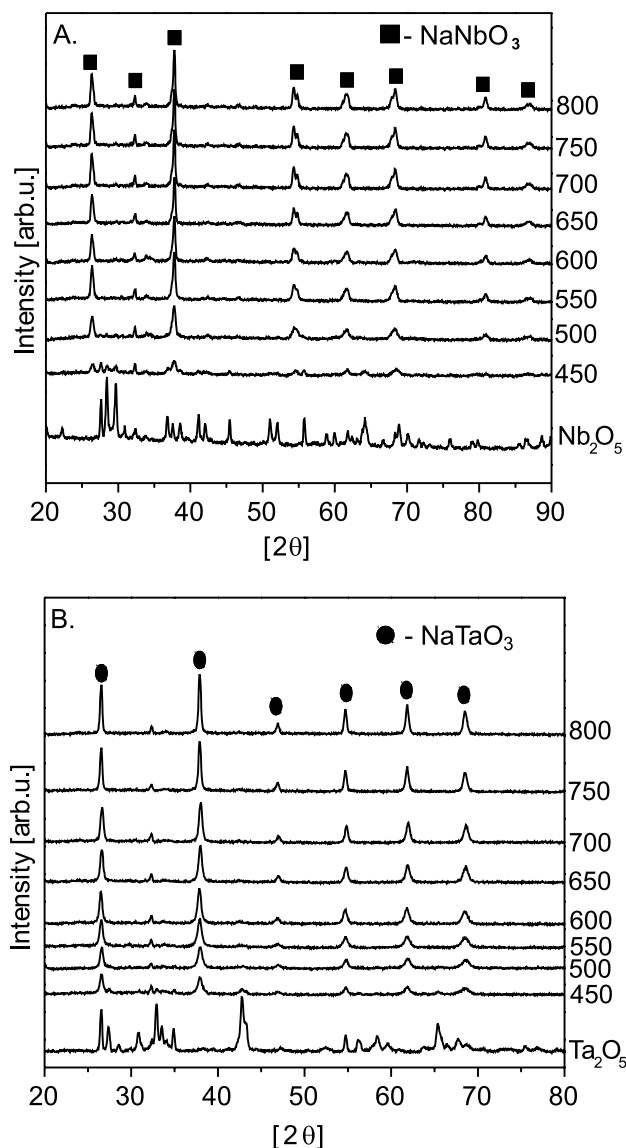
The crystalline structures of the catalysts were characterized by X-ray diffraction (XRD) analysis (X'Pert PRO Philips diffractometer) using  $\text{CoK}\alpha$  radiation. The photocatalytic and optical properties of the prepared photocatalysts were investigated by means of Diffuse Reflectance Ultraviolet Visible (DR-UV-vis) technique using a Jasco (Japan) spectrometer. The Planck equation was used for the calculation of the value of the prepared catalysts band gap<sup>6</sup>. The BET surface areas and mean pore diameters of the catalysts were determined by the nitrogen gas adsorption method using a Micrometrics ASAP 2010 device.

The activities of the obtained catalysts for the photocatalytic reactions of hydrogen generation were carried out in a close system with an inner-irradiation-type reactor. As a light source a medium pressure mercury lamp of 150 W was used. The photocatalyst powder was dispersed in an aqueous organic donor solution (0.8 dm<sup>3</sup>). Formic acid was used as a model organic donor. The suspension was mixed with the magnetic stirrer for 1 hour, and during that time argon was being bubbled through the reaction mixture to remove the oxygen content. Later, the solution was irradiated for two hours without argon purge. The reaction was carried out at a room temperature. The amount of evolved hydrogen was determined by using a gas chromatograph (The Thermal Conductivity Detector (TCD), Ar as a gas carrier).

## RESULTS AND DISCUSSION

Fig. 1A and B show the XRD patterns of the catalysts produced after calcination of niobium or tantalum

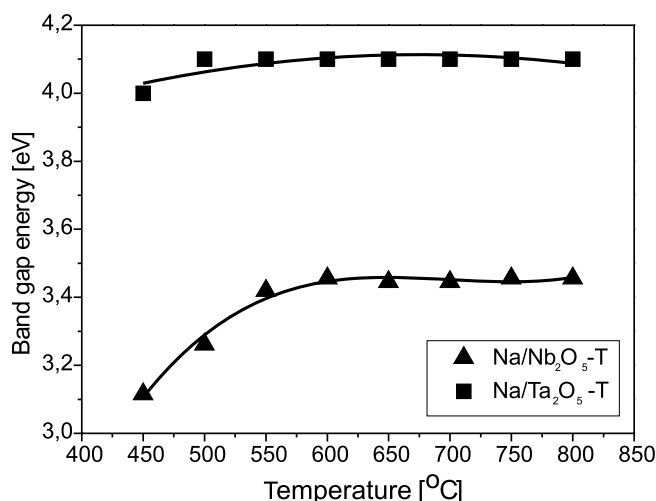
pentaoxides with sodium hydroxide at different temperature ranges from 450°C to 800°C as well as patterns of the pristine Nb<sub>2</sub>O<sub>5</sub> (Fig. 1A) and Ta<sub>2</sub>O<sub>5</sub> (Fig. 1B). From Fig. 1A and 1B it is clearly seen that NaNbO<sub>3</sub> and NaTaO<sub>3</sub> phases started to appear at the temperature of 450°C (Na/Nb<sub>2</sub>O<sub>5</sub>-450 and Na/Ta<sub>2</sub>O<sub>5</sub>-450). Additionally, it can be stated that in the case of both those samples the diffraction peaks of Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> can also be simultaneously detected. Additionally, it can be noticed that when the temperature of calcination increases from 500 to 800°C the intensity of diffraction peaks becomes stronger and NaNbO<sub>3</sub> and NaTaO<sub>3</sub> are the main phase of Na/Nb<sub>2</sub>O<sub>5</sub>-T and Na/Ta<sub>2</sub>O<sub>5</sub>-T catalysts, respectively.



**Figure 1.** A comparison of X-ray diffraction patterns of the pristine Nb<sub>2</sub>O<sub>5</sub> (A.) and Ta<sub>2</sub>O<sub>5</sub> (B.) and produced Na/Nb<sub>2</sub>O<sub>5</sub>-T (A.) and Na/Ta<sub>2</sub>O<sub>5</sub>-T (B.) photocatalysts at different temperatures of calcination

The band gap energy (EG) of the pristine Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> obtained from the optical absorption edge are about 3.07 eV and 3.93 eV, respectively. In the case of Na/Nb<sub>2</sub>O<sub>5</sub>-T catalysts when the temperature of calcination increases from 450°C to 600°C, band gap energies widely increase from 3.12 eV (Na/Nb<sub>2</sub>O<sub>5</sub>-450) to 3.45 eV (Na/Nb<sub>2</sub>O<sub>5</sub>-600). Further increase of the calcination temperature (650 – 800°C) did not cause the change of EG of the

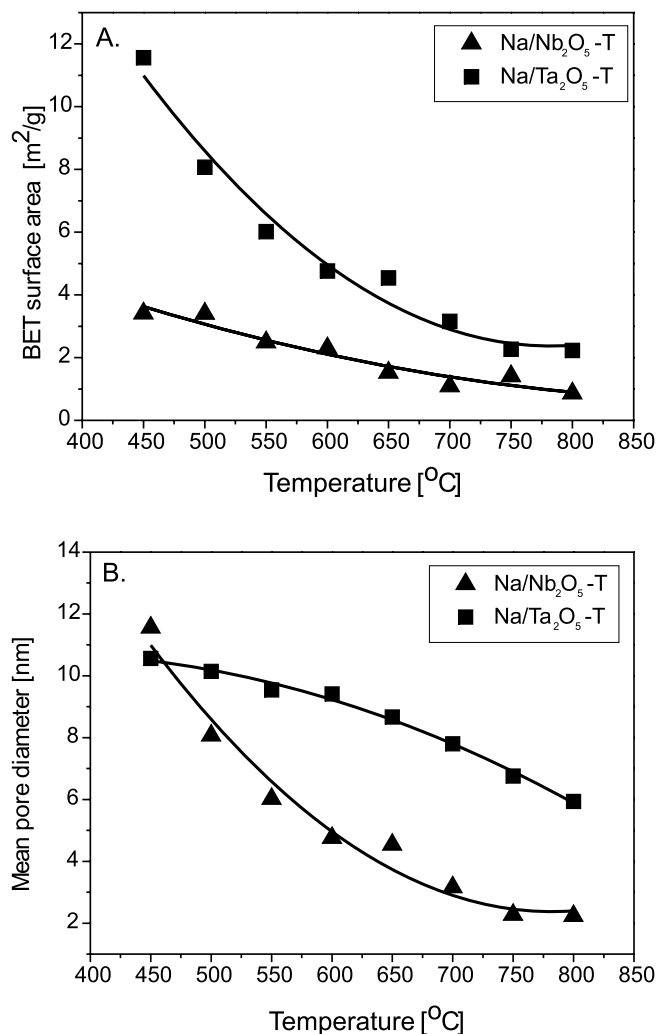
produced materials. Band gap energies of Na/Nb<sub>2</sub>O<sub>5</sub>-650, Na/Nb<sub>2</sub>O<sub>5</sub>-700, Na/Nb<sub>2</sub>O<sub>5</sub>-750 and Na/Nb<sub>2</sub>O<sub>5</sub>-800 are about 3.45 eV. In the case of Na/Ta<sub>2</sub>O<sub>5</sub>-T photocatalysts, EG did not change with the increase of the calcination temperature. For all Na/Ta<sub>2</sub>O<sub>5</sub>-T materials calculated band gap energies equaled about 4.1 eV. Additionally, one can notice that calculated band gap energies of Na/Nb<sub>2</sub>O<sub>5</sub>-T and Na/Ta<sub>2</sub>O<sub>5</sub>-T samples are identical to those described in the literature. The band gap energies of NaNbO<sub>3</sub> and NaTaO<sub>3</sub> obtained from the optical absorption edge range from 3.08 to 3.5 eV and 3.9 to 4.1 eV, respectively<sup>6-12</sup>.



**Figure 2.** Band gap energies of Na/Nb<sub>2</sub>O<sub>5</sub>-T and Na/Ta<sub>2</sub>O<sub>5</sub>-T photocatalysts

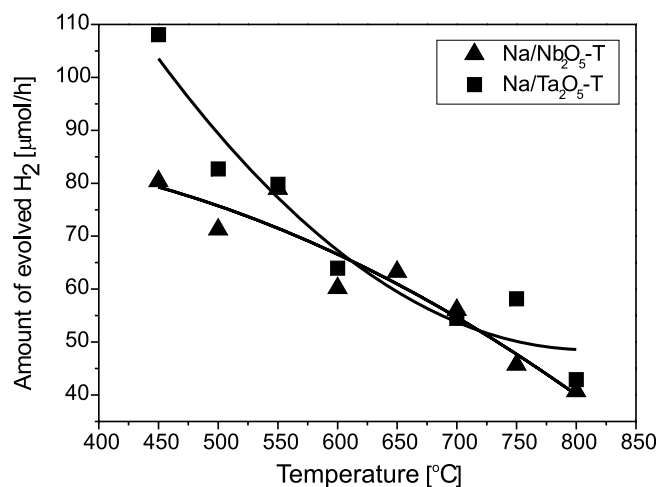
Other characteristic parameters such as BET surface area and a mean pore diameter of the produced photocatalysts (Na/Nb<sub>2</sub>O<sub>5</sub>-T and Na/Ta<sub>2</sub>O<sub>5</sub>-T) have also been measured. According to the manufacturer's data, Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> have a small specific surface area of 0.76 m<sup>2</sup>/g and 1.34 m<sup>2</sup>/g and a mean pore diameter of 5.25 nm and 10.08 nm, respectively. The comparison of BET surface areas and mean pore diameters of the produced photocatalysts is presented in Fig. 3. We observed that the modification of Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> with NaOH caused the increase of BET surface areas. For example, BET surface area of Na/Nb<sub>2</sub>O<sub>5</sub>-450 and Na/Ta<sub>2</sub>O<sub>5</sub>-450 are about 4.5 and 8 times higher than those of the pristine Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub>, respectively. Moreover, from Fig. 4 it is clearly seen that those both parameters decrease with the increase of calcination temperature from 450 to 800°C.

The photocatalytic activities of the obtained materials (Na/Nb<sub>2</sub>O<sub>5</sub>-T and Na/Ta<sub>2</sub>O<sub>5</sub>-T) have been studied in the reaction of hydrogen generation. The experiments were conducted in the presence of formic acid as a model organic donor. The concentration of HCOOH (0.1 M) and the weight of the catalyst (0.2g) were kept the same for all reactions. The comparison of hydrogen evolution over the studied photocatalysts is presented in Fig. 4. From the obtained results it is clearly seen that for both Na/Nb<sub>2</sub>O<sub>5</sub>-T and Na/Ta<sub>2</sub>O<sub>5</sub>-T photocatalysts the amount of released hydrogen decreases when the calcination temperature increases from 450 to 800°C. For example, the amount of released hydrogen decreases from 80 μmol/h to 41 μmol/h in the case of Na/Nb<sub>2</sub>O<sub>5</sub>-T catalysts and from 108 μmol/h to 43 μmol/h for Na/Ta<sub>2</sub>O<sub>5</sub>-T materials. Additionally, it can be stated that among all studied



**Figure 3.** BET surface areas (A.) and mean pore diameters (B.) of Na/Nb<sub>2</sub>O<sub>5</sub>-T and Na-Ta<sub>2</sub>O<sub>5</sub>-T photocatalysts

photocatalysts the highest photocatalytic activity was observed for the Na-Ta<sub>2</sub>O<sub>5</sub>-450. It indicated that the catalyst with the highest surface area (11.63 m<sup>2</sup>/g, Na-Ta<sub>2</sub>O<sub>5</sub>-450) exhibited the highest photocatalytic activity.



**Figure 4.** The photocatalytic hydrogen evolution over Na/Nb<sub>2</sub>O<sub>5</sub>-T and Na-Ta<sub>2</sub>O<sub>5</sub>-T photocatalysts using formic acid solution (HCOOH concentration – 0.1M, amount of catalysts – 0.2 g)

## CONCLUSIONS

In summary, sodium niobate and tantalate (NaNbO<sub>3</sub> and NaTaO<sub>3</sub>) were synthesized by the impregnation of

Nb<sub>2</sub>O<sub>5</sub>/Ta<sub>2</sub>O<sub>5</sub> in the aqueous solution of sodium hydroxide and then calcination at the temperature range of 450 – 800°C. The photocatalytic activities of the produced photocatalysts were examined in the reaction of photocatalytic hydrogen generation.

To conclude, among all studied catalysts (niobates and tantalates), the highest photocatalytic activity was observed for the samples named Na-Ta<sub>2</sub>O<sub>5</sub>-450. The value of 108 µmol H<sub>2</sub>/h was detected.

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