



## Synthesis and Photocatalytic Properties of Silver Niobate

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The interaction between silver nitrate and niobium pentoxide has been studied under conventional thermal treatment (TT) as well as mechanochemical and sonochemical treatment (MChT and UST, respectively). The products of reaction have been investigated using XRD, DTA-TG, Raman spectroscopy, adsorption of nitrogen. MChT and UST promote lowering the temperature of silver niobate (SN) formation. The formed SN possesses higher specific surface area and photocatalytic activity.

**Keywords:** Silver Niobate, Milling, Sonochemical Treatment, Photocatalytic Activity.

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### 1. INTRODUCTION

The development of photocatalysts with visible-light response has been studied extensively from the viewpoint of the utilization of solar light energy including for degradation of pollutants in air and water. Such ferroelectric material as silver niobate  $\text{AgNbO}_3$  possessing the perovskite structure is a potential photocatalyst [1, 2]. The  $\text{AgNbO}_3$  samples were usually prepared using a solid-state reaction method by mixing powders of  $\text{Ag}_2\text{O}$  and  $\text{Nb}_2\text{O}_5$  in nonstoichiometric ratio, followed by a pre-heat treatment at 800 °C for 4 h and then calcination at 970 °C for 7 h in air [3]. In this work, we studied the influence of preliminary sono- and mechanochemical activation of reaction mixture  $\text{AgNO}_3 + \text{Nb}_2\text{O}_5$  on structure and catalytic properties of  $\text{AgNbO}_3$ .

### 2. EXPERIMENTAL PROCEDURE

#### 2.1 Silver niobate synthesis

Silver nitrate and niobium pentoxide with different specific surface area (2 and 355  $\text{m}^2 \cdot \text{g}^{-1}$ ) were used as initial reagents. These mixtures were subjected to ultrasound and mechanochemical treatment (UST and MChT, respectively) in water and air. Activated products (precursors) were additionally calcined at 450 and 600 °C.

#### 2.2 Physical-chemical characterization

The phase composition was studied by means of X-ray powder diffraction (XRD) using Philips PW 1830 diffractometer with  $\text{CuK}_\alpha$ -radiation. The primary crystallites size  $D_{\text{hkl}}$  was calculated using the broadening of the most intensive lines according to Sherrer's equation. Curves of DTA and TG were recorded using Derivatograph-C apparatus (F.Paulik, J.Paulik, L.Erdey) in the range of temperature 20-600 °C at the heating rate 10°/min. Initial mass of sample was 200 mg. Diffuse reflectance UV-Vis spectra of powders were registered on Lambda 35 UV-Vis spectrometer (Labsphere RSA-

PE-20 diffuse reflectance and transmittance accessory, Perkin-Elmer Instruments).  $\text{BaSO}_4$  was used as a reference. All spectra are presented in coordinates of Kubelka-Munk equation. Parameters of porous structure (specific surface area  $S$ , total pore volume  $V_\Sigma$ , sorption pore volume  $V_s$  and volume of mesopores  $V_{\text{me}}$ ) were determined from isotherms of nitrogen adsorption-desorption obtained with the help of ASAP 2405N analyzer ("Micromeritics Instrument Corp").

#### 2.3. Catalytic activity

The testing of photocatalytic activity was carried out using degradation of Rhodamine B (Rh B) in aqueous medium ( $0.5 \cdot 10^{-5} \text{ mol L}^{-1}$  solution). This reaction was performed in glass reactor with magnetic stirrer. The illumination was realized using high-intensity discharge Na lamp GE Lucalox (Hungary) with power 70 W which irradiates solely in visible region. The ratio catalyst/dye solution was 100 mg/150 ml and 100 mg/50 ml during visible and UV-illumination, respectively. The initial solution and that after dye degradation was analyzed spectrophotometrically at  $\lambda_{\text{max}} = 555 \text{ nm}$  (Lambda 35, PerkinElmer Instruments) after centrifugation of reaction mixture (10 min at 8000 rpm). The calculation of photodegradation rate constants  $K_d$  was based on the concentration change of the solution after establishment of adsorption/desorption equilibrium. The samples of silver niobate were also tested as catalysts in mechanochemical degradation of Rh B in solution ( $0.005 \text{ g L}^{-1}$ ).

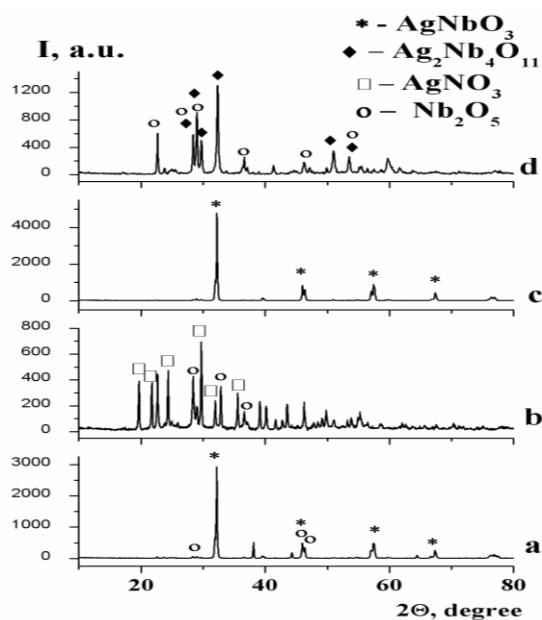
### 3. RESULTS AND DISCUSSION

#### 3.1 Phase composition

XRD and DTA-TG data show that silver niobates do not formed on the stage of modification. However, crystallinity of reagents is changed. Thus, UST causes complete amorphization of reagents. At the same time, crystal structure of both components is partially destroyed as a result of MChT. Both results can be estimated as preparation of activated precursors. Indeed,

the next calcinations of obtained precursors results in facilitation of interaction between components as well as formation of pure niobates.

Pure silver niobate does not formed from initial (non-activated) mixture after its annealing at 700°C: reflexes of Nb<sub>2</sub>O<sub>5</sub> are presented on diffractogram (Fig. 1, curve a).

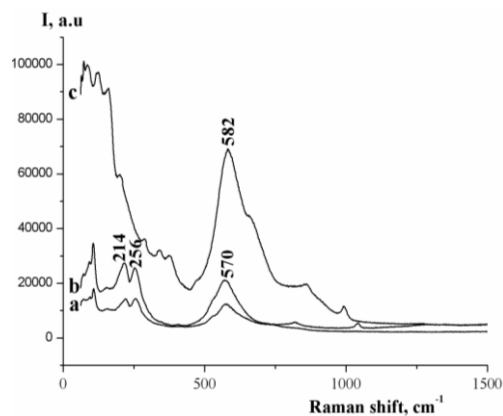


**Fig. 1** – XRD patterns of AgNO<sub>3</sub>+Nb<sub>2</sub>O<sub>5</sub> mixture: initial mixture after calcined at 700 °C (a), after MChT in air at 850 rpm (b), the same after calcined at 450 °C (c), after MChT in water at 850 rpm and calcined at 600 °C (d)

For example, sonochemical precursor is X-ray amorphous although its calcinations at 600 °C cause appearance of crystalline silver niobate. However, thermal treatment of precursor prepared through dry milling leads to formation of silver niobate AgNbO<sub>3</sub> at 450 °C (curve c). Elevation of temperature results in improvement of crystal structure of AgNbO<sub>3</sub>. Crystallite size D<sub>020</sub> increases from 17 to 21 nm. On the other hand, bi-phase product is formed in the same conditions from precursor activated via milling in water. These are Ag<sub>2</sub>Nb<sub>4</sub>O<sub>11</sub> (prevalent phase) and Nb<sub>2</sub>O<sub>5</sub> (curve d). Content of niobate and its crystallite size also increases after calcinations at higher temperature. Raman spectra of calcined samples additionally exhibit differences in their structure (Fig. 2, curves a and b): there are three bands attributed to AgNbO<sub>3</sub> around 214, 256, 570 cm<sup>-1</sup> [4]. These peaks are absent on spectrum of sample prepared from milled in water precursor. The latter sample contains another niobate, namely Ag<sub>2</sub>Nb<sub>4</sub>O<sub>11</sub>.

**Table 1** – Some properties of silver niobate samples

N	Modification conditions	S, m <sup>2</sup> ·g <sup>-1</sup>	V <sub>Σ</sub> , cm <sup>3</sup> ·g <sup>-1</sup>	V <sub>s</sub> , cm <sup>3</sup> ·g <sup>-1</sup>	V <sub>me</sub> , cm <sup>3</sup> ·g <sup>-1</sup>	K <sub>d</sub> ·10 <sup>5</sup> , s <sup>-1</sup>
1	2	3	4	5	6	7
1	(AgNO <sub>3</sub> +Nb <sub>2</sub> O <sub>5</sub> ) TT 700°C	4.1	0.50	0.05	0.05	0.81
2	(Ag NO <sub>3</sub> +Nb <sub>2</sub> O <sub>5</sub> ) MChT 850 rpm air	2.8	0.01	0.005	0.005	-
3	(AgNO <sub>3</sub> +Nb <sub>2</sub> O <sub>5</sub> ) MChT 850 rpm air+TT 450°C	6.8	0.03	0.01	0.01	3.90
4	(AgNO <sub>3</sub> +Nb <sub>2</sub> O <sub>5</sub> ) MChT 850 rpm air+TT 600°C	4.5	0.01	0.005	0.01	1.27/3 7.5*



**Fig. 2** – Raman spectra for AgNO<sub>3</sub>+Nb<sub>2</sub>O<sub>5</sub> mixture: initial mixture after calcined at 450 °C (a), after MChT in air and calcined at 600 °C (b), after MChT in water and calcined at 600 °C (c)

### 3.2 Porous structure

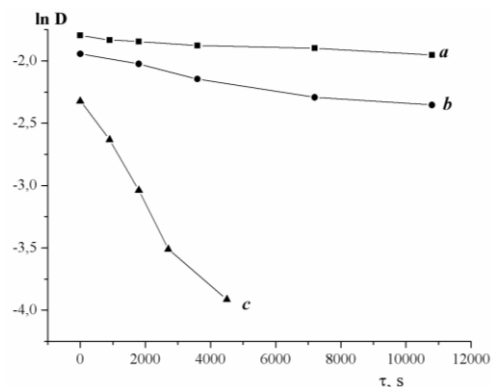
The specific surface area and parameters of porous structure of prepared silver niobate can be varied when conditions of modification and next calcinations are changed. Thus, milling in water and air enables to prepare sample with increased S compared to that synthesized by means of conventional solid state interaction (Table, samples NN1-7). Thus, specific surface area of sample milled in water and calcined at 450 °C reaches 8 m<sup>2</sup>·g<sup>-1</sup> while “solid state” samples has S = 4.1 m<sup>2</sup>·g<sup>-1</sup>. The use of high-dispersed Nb<sub>2</sub>O<sub>5</sub> and ultrasound treatment allow to obtain macro-mesoporous samples possessing high values S and V<sub>me</sub> (samples NN8-10).

### 3.3 Catalytic activity

The samples of silver niobate prepared from mechanochemical and sonochemical precursors also exhibit higher photocatalytic activity in process of rhodamine B degradation under UV- and visible light. This shows the kinetic curves, expressed on Fig. 3, and the rate constant of degradation under visible irradiation, values of which are presented in column 7 of Table. Besides, one can see a clear dependence between K<sub>d</sub> and value of specific surface area which is characteristic for photocatalytic properties, as a rule [5]. Similarly, the rate constant of mechanocatalytic degradation of Rh B increases with increasing of specific surface area of catalyst (silver niobate). The values of K<sub>d</sub> for this process are higher than ones obtained for visible photocatalytic degradation and equal within 2.3-5.3 10<sup>-4</sup> s<sup>-1</sup>.

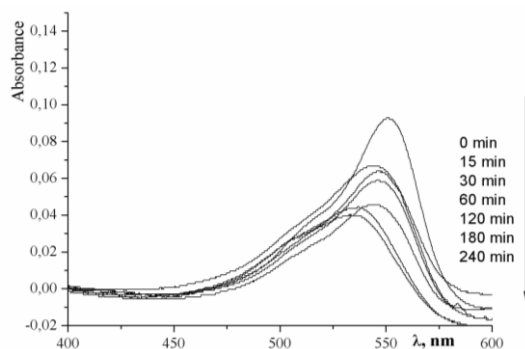
1	2	3	4	5	6	7
5	(Ag NO <sub>3</sub> +Nb <sub>2</sub> O <sub>5</sub> ) MChT 850 rpm water	5.4	0.21	0.01	0.01	-
6	(AgNO <sub>3</sub> +Nb <sub>2</sub> O <sub>5</sub> ) MChT 850 rpm water+TT 450°C	8.0	0.28	0.02	0.02	5.5
7	(AgNO <sub>3</sub> +Nb <sub>2</sub> O <sub>5</sub> ) MChT 850 rpm water+TT 600°C	6.7	0.20	0.005	0.01	2.39
8	(Ag NO <sub>3</sub> +Nb <sub>2</sub> O <sub>5</sub> ) UST 2 h	156	0.93	0.26	0.25	6.32
9	(Ag NO <sub>3</sub> +Nb <sub>2</sub> O <sub>5</sub> ) UST 2 h+TT 450°C	93	0.62	0.18	0.19	3.16
10	(Ag NO <sub>3</sub> +Nb <sub>2</sub> O <sub>5</sub> ) UST 2 h+TT 600°C	45	0.51	0.14	0.14	2.03

\*- under UV-irradiation



**Fig. 3** – Kinetic curves of photocatalytic Rh B degradation in the presence of AgNO<sub>3</sub>+Nb<sub>2</sub>O<sub>5</sub> after MChT in air and calcined at: 600 °C (a) and 450 °C (b) under visible irradiation, 600 °C under UV-irradiation (c)

Noteworthy that shift of band at 555 nm (about 10 nm) towards shorter wavelengths (namely, to 545 nm) is observed on spectra of Rh B solution after the first 15 min of UV- and visible photocatalytic degradation (for example, Fig. 4).



**Fig. 4** – UV-Vis spectral changes of Rhodamin B aqueous solution in the presence of AgNbO<sub>3</sub> after MChT at 850 rpm in water and calcined at 450 °C (sample N6) after visible irradiation

This corresponds to formation of N,N-diethyl-N'-ethyl-rhodamine 110 (intermediate) as a result of deethylation of Rh B [6]. The cleavage of chromoforic ring obviously takes place later which leads to reduction of band 545 nm intensity. The further shift to 535 nm is observed after 180-240 min. On the other hand, such shift does not revealed in spectra of Rh B solutions after mechanochemical degradation for the same time. Meanwhile, only decrease of band at 555 nm occurs.

#### 4. CONCLUSION

Mechano- and sonochemical activation allow to lower (compared to conventional solid state reaction) temperature of interaction of AgNO<sub>3</sub> and Nb<sub>2</sub>O<sub>5</sub> with formation of silver niobates. Milling in air promotes formation of AgNbO<sub>3</sub> while milling in water results in appearance of Ag<sub>2</sub>Nb<sub>4</sub>O<sub>11</sub> phase. The formed niobates possess higher specific surface area and photocatalytic and mechanocatalytic activity in process of rhodamine B degradation, as a result.

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