ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2011, Vol. 56, No. 11, pp. 1693–1697. © Pleiades Publishing, Ltd., 2011. Original Russian Text © A.V. Gorokhovsky, I.D. Kosobudskii, E.V. Tret'yachenko, G.Yu. Yurkov, L.V. Nikitina, A.I. Palagin, 2011, published in Zhurnal Neorganicheskoi Khimii, 2011, Vol. 56, No. 11, pp. 1775–1780.

> SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

# Potassium Polytitanates Intercalated with Nickel Ions and Their Thermal Transformations

A. V. Gorokhovsky<sup>*a*</sup>, I. D. Kosobudskii<sup>*a*</sup>, E. V. Tret'yachenko<sup>*a*</sup>, G. Yu. Yurkov<sup>*b*</sup>, L. V. Nikitina<sup>*a*</sup>, and A. I. Palagin<sup>*c*</sup>

<sup>a</sup> Saratov State Technical University, ul. Universitetskaya 42, Saratov, 410601 Russia
<sup>b</sup> Baikov Institute of Metallurgy, Russian Academy of Sciences, Leninskii pr. 49, Moscow, 119991 Russia
<sup>c</sup> Science and Production Company Nanocomposite, Saratov, Russia

Received October 14, 2010

**Abstract**—The intercalation of nickel ions into the layered structure of ultradispersed amorphous potassium polytitanate powder on treatment with an aqueous solution of nickel sulfate was studied. The limiting nickel content that can be attained by intercalation is 12.8 wt %. The nickel ion intercalation results in a decrease in the average particle size of potassium polytitanate and in the structural ordering. Heat treatment of the resulting intercalate promotes the formation of a nanocomposite consisting of the solid solution  $K_{1.35}(Ni_xTi_{8-x})O_{16}$  with the hollandite structure,  $Ti_2O_3$ , and, depending on the treatment schedule, either NiO nanocrystals or Ni metal.

DOI: 10.1134/S0036023611110088

## THEORETICAL ANALYSIS

During the last decade, particular interest is aroused by the synthesis of mesoporous materials that exhibit high adsorption properties in combination with the catalytic activity [1-3]. The synthesis of mesoporous transition metal oxides having a number of advantages due to the high catalytic activity is hampered as a result of high rate of hydrolysis of transitionmetal ions and their tendency to form structures with large coordination numbers [2].

A convenient method for solving this problem is intercalation of transition metals into the structure of layered minerals functioning as supports [4–7]. The use of layered titanium oxide modifications and its derivatives for this purpose provides the possibility of forming various types of structures with enhanced catalytic activities: titanates intercalated with transitionmetal ions; doped titanates in which some titanium atoms are replaced by transition-metal atoms; combined structures consisting of layers of a semiconductor with relatively wide band gap (titanium oxide) and a semiconductor with a relatively narrow band gap (transition metal oxide).

It should be borne in mind that titanates doped with transition metals exhibit photocatalytic activity in the visible region [4, 5, 7], which is especially important, as the total intensity of solar radiation in the UV region (the region of TiO<sub>2</sub> photoactivity) is only 4-6%, whereas in the visible region it increases to 45% [8].

On the other hand, each of the listed types of catalytic systems has its own advantages and drawbacks.

Thus alkali metal titanates with intercalated transition-metal ions have a number of advantages over the titanium oxide-transition metal oxide composite systems; localization of the positively charged transitionmetal ions in the interlayer space of the polyanions formed by titanium-oxygen polyhedra brings about a much broader pH range in which the stability of these structures is maintained [8-10]. However, there are only few works devoted to the use of intercalation synthetic processes for the preparation of high-performance catalytic systems in which layered titanates are used as matrices. In particular, it was shown [11] that nickel doping of hydrated titanium oxide increases its photocatalytic activity. The kinetics of ion-exchange adsorption of nickel with hydrated titanium oxide was measured [12]. In addition, it was noted [13] that initial layered potassium tetratitanate has a higher catalytic activity in the photocatalytic reduction of Cr(VI)to Cr(III) than protonated potassium tetratitanate.

The interlayer spacing in layered crystalline potassium titanates is relatively small; this hampers the penetration of multicharged ions into it. Therefore, to increase the sorption capacity with respect to transition-metal ions, it is necessary to intercalate first larger organic cations [14]. Potassium polytitanates look more attractive as matrix materials for intercalation of transition-metal ions. The class of potassium polytitanates having amorphous or highly distorted crystal structure consisting of layers located far apart was synthesized rather recently [15] and exhibited very high sorption characteristics with respect to Pb(II) ions [16].



**Fig. 1.** X-ray diffraction patterns of potassium polytitanate (1) before and (2) after intercalation of nickel ions.

The purpose of this work is an attempt at intercalation of nickel(II) ions into the potassium polytitanate structure from aqueous solutions of nickel salts and study of the processes taking place during the heat treatment of the intercalates.

### **EXPERIMENTAL**

Potassium polytitanate (PPT) was prepared by a published procedure [15]. Powdered TiO<sub>2</sub> (anatase, 99%+ purity, average particle size 3  $\mu$ m, Aldrich) was placed in an alundum crucible containing a melt of a KOH and KNO<sub>3</sub> mixture (99%+ purity, Aldrich). The composition of the reaction mixture was as follows (wt %): TiO<sub>2</sub> (10), KOH (10), KNO<sub>3</sub> (80). The crucible with the reaction mixture was kept at 500°C for 2 h and then the contents was placed in water. The resulting powder was washed with distilled water at water : melt = 20 : 1 (w/w) to remove the remaining water-soluble components of the raw material mixture and products. Then it was filtered (Whatman no 42 filter paper) and dried in a drying oven at 60°C for 6 h.

The PPT powder thus formed (a 10-g portion) was placed in a vessel maintained at 23°C by a thermostat and containing a 0.01 M aqueous solution of NiSO<sub>4</sub>  $\cdot$  $7H_2O$  taken to make 10 g of potassium polytitanate per 0.05 mol of Ni present in the solution. The resulting suspensions were magnetically stirred for different periods of time (from 1 to 18 h) and then filtered using Wathman-42 filter paper. The powders obtained upon filtration were dried for 4 h at 60°C and heat-treated in order to obtain a thermodynamically stable structure. The heat treatment was carried out in air using two temperature schedules. According to schedule I, the precursor material (amorphous potassium polytitanate with intercalated nickel ions) was heated at 10 K/min to 850°C and kept at this temperature for 1 h. The treatment temperature was chosen proceeding from the fact that amorphous potassium polytitanate was reported to crystallize at 800-850°C to give a mixture of fibrous potassium tetra- and hexatitanate crystals [15]. In addition, heat treatment was also carried out using a two-stage schedule including pretreatment of the intercalate at a temperature of  $350^{\circ}$ C at which molecular water was reported to be completely removed from potassium polytitanate [15]. The intercalate powder was heated to  $350^{\circ}$ C at 10 K/min, kept at this temperature for 1 h, and then the sample was heated to  $850^{\circ}$ C at 10 K/min and kept there for 1 h for phase-formation processes to be completed.

The powders obtained after heat treatment were studied by scanning electron microscopy (an ESEM Philips XL-30 electron microscope equipped by a EDS Pegasus local X-ray microanalysis attachment) and powder X-ray diffraction (DRON-4 diffractometer, a tube with a copper anode). The X-ray diffraction patterns were interpreted using a PCPDFWIN database (v.2.02, 1999).

## **RESULTS AND DISCUSSION**

X-ray diffraction patterns and electron microscopic images of the potassium polytitanate powder particles containing nickel intercalated from a nickel sulfate solution before and after the heat treatment according to different schedules are shows in Figs. 1, 2 and 3, 4, respectively.

The obtained data indicate that the X-ray diffraction pattern of potassium polytitanate intercalated with nickel from a nickel sulfate solution is typical of quasi-amorphous materials with very high degrees of defectiveness of the crystal structure (Fig. 1) and differs little from the X-ray diffraction pattern of the starting PPT. However, whereas the initial potassium polytitanate is white, the powder obtained after treatment in a nickel salt solution has a light green color, indicating the insertion of Ni<sup>2+</sup> ions in the PPT structure. Note also that nickel-intercalated samples of potassium polytitanate (Fig. 1) show a clear-cut peak at small  $2\theta$  angles (9.8°), indicating that the interplanar spacing in the layered structure of potassium polytitanate becomes a constant value after intercalation. In addition, during treatment of PPT in an aqueous solution of nickel salt, the particle size decreases (Fig. 3), probably, due to hydrolysis, which is confirmed by the increase in the pH of the aqueous solution during treatment (from 5.7 to 9.3).

The limiting capacity of potassium polytitanate in the ion-exchange adsorption of nickel ions is about 14.8 wt % (Fig. 5), it is achieved after 6 h of the contact with an aqueous solution of nickel sulfate. The subsequent keeping of potassium polytitanate in the solution has almost no effect on the Ni content in PPT but somewhat decreases the content of potassium as the hydrolysis of potassium polytitanate continues, although slowly. Therefore, all of the subsequent experiments dealing with the behavior of intercalates upon heat treatment were performed using the potassium polytitanate sample treated in aqueous solution of nickel sulfate at room temperature for 6 h. According to the local X-ray microanalysis data, this product





**Fig. 2.** X-ray diffraction patterns of nanocomposites obtained after intercalation and heat treatment of potassium polytitanate in (*a*) two-stage and (*b*) one-stage schedules. Phases: (1) potassium hollandite, (2) NiO, (3) Ni, and (4)  $Ti_2O_3$ .

had the following composition (wt %): Ti (45.4), K (2.7), Ni (14.6), O (36.3), S (1.1).

The heat treatment of the nickel-intercalated potassium polytitanate brings about different effects depending on whether one- or two-stage heat treatment schedule was used. In the case of one-stage schedule (treatment at 850°C), a crystal structure identical to the  $K_{1.35}Ti_8O_{16}$  is formed (IPDD 47-0690 card, potassium hollandite). In addition, the X-ray diffraction patterns of the powders obtained using a one-stage schedule contain peaks corresponding to the nickel metal. It is curious that this powder is colored bright-yellow, and this attests that its electronic structure differs sharply from the precursor (intercalate) structure, which is light light green.

On the other hand, the X-ray diffraction patterns of the product obtained using the two-stage schedule of heat treatment of the precursor material  $(350^{\circ}C + 850^{\circ}C)$  exhibit no peaks corresponding to nickel metal (Fig. 2); however, there are peaks corresponding to NiO. The product after annealing is colored yellowish green.

It is important that both products of the heat treatment of PPT intercalated with nickel ions are composed of ultradispersed particles of nonuniform chemical composition, i.e., these are composite nanomaterials (Fig. 4). The nanosized Ni and NiO crystals formed upon the heat treatment of the precursor are located on the surface and in the interlayer space of the layered crystalline matrix. Note that the particle morphologies of nanocomposites obtained using one- and two-stage schedules are different (Fig. 4).

Alkali metal titanates with defective crystal lattices possess a reducing capacity due to the rather high content of titanium as  $Ti^{3+}$  [17]. The titanium–oxygen

polyhedra formed by five-coordinated titanium ions (regular tetrahedral pyramids) in rutile type oxides usually form chains known as extended Wadsley defects [18].

Thus, presumably, two redox processes take place in parallel in potassium polytitanate intercalated with nickel ions during the heat treatment.

During the first process, which is localized at the chains (extended Wadsley defects) composed of regular tetrahedral pyramids (five-coordinated titanium atoms), these chains are converted to chains consisting of titanium–oxygen octahedra (six-coordinated titanium atoms), and the reduced nickel atoms form Ni clusters in the interlayer space:

$$2\text{Ti}(3+) + \text{Ni}(2+) = 2\text{Ti}(4+) + \text{Ni}(0).$$

During the second process that occur at the PPT chains consisting of titanium—oxygen octahedra (sixcoordinated titanium atoms), these are transformed to titanium—oxygen polyanions consisting of regular tetrahedral pyramids (five-coordinated titanium atoms). During the annealing, linear titanium—oxygen polyanions are transformed to more compact  $Ti_2O_3$  nanocrystals. The nickel ions, which were initially located in the interlayer space, are embedded in the polyanionic chains composed of six-coordinated transition-metal atoms (titanium—oxygen and nickel—oxygen octahedra), their negative charge being counterbalanced by the K<sup>+</sup> cations:

$$2\text{Ti}(4+) + \text{Ni}(2+) = 2\text{Ti}(3+) + \text{Ni}(4+).$$

Thus, the product of one-stage heat treatment of PPT (850°C/1 h) intercalated with nickel ions consists of the solid solution particles  $K_{1,35}(Ni_xTi_{8-x})O_{16}$  having a hollandite structure with inclusions of Ti<sub>2</sub>O<sub>3</sub> nanoc-



**Fig. 3.** TEM images of potassium polytitanate particles (a) before and (b) after intercalation of Ni ions.

rystals in which the titanium atoms are five-coordinated. The mesopores of the obtained structures accommodate Ni metal nanocrystals.

Since the powders are annealed in air, the processes that take place in the system are affected to a greater extent by atmospheric oxygen when heat-treated in the two-stage schedule ( $350^{\circ}C/1 h + 850^{\circ}C/1 h$ ). The nickel atoms in the interlayer space of potassium polytitanate are vigorously oxidized to give the new nickel oxide (NiO) phase; furthermore, some of Ti(3+) present in Ti<sub>2</sub>O<sub>3</sub> is converted to Ti(4+), which is incorporated into the hollandite structure, as indicated by the decrease in the intensity of T<sub>2</sub>O<sub>3</sub> peaks relative to the K<sub>1.35</sub>(Ni<sub>x</sub>Ti<sub>8-x</sub>)O<sub>16</sub> hollandite peaks in the X-ray diffraction patterns.

Since the diffraction peaks of NiO in the X-ray diffraction patterns of the product formed in the twostage heat treatment are substantially stronger than the Ni peaks in the X-ray diffraction patterns of the onestage heat treatment product, presumably, in the latter



**Fig. 4.** Electron microscopic images of powder particles obtained after heat treatment of potassium polytitanate intercalated with  $Ni^{2+}$  ions according to (a) two-stage and (b) one-stage schedules.

case, some nickel atoms are located in the interlayer space of hollandite-like structures as very small atomic clusters, i.e., this form is amorphous to X-rays. A similar situation was observed in our previous work dealing with the synthesis of polymer matrix composites containing Ni nanoparticles [19].

In summary, we studied intercalation of nickel ions into the layered structure of amorphous potassium polytitanate. It was shown that the maximum content of nickel intercalated into the structure of an ultradispersed potassium polytitanate powder from a saturated aqueous solution of NiSO<sub>4</sub> · 7H<sub>2</sub>O at 23°C is observed after 6 h of the contact; the limiting Ni concentration in the intercalate is ~15 wt %. The nickel intercalation promotes ordering of the potassium polytitanate structure and decrease in the particle size. The heat treatment of potassium polytitanate intercalated with nickel ions gives rise to ceramic composite material consisting of the K<sub>1.35</sub>(Ni<sub>x</sub>Ti<sub>8-x</sub>)O<sub>16</sub> solid solution with



**Fig. 5.** Kinetics of variation of the concentrations of elements during intercalation of nickel ions from aqueous solution into a potassium titanate powder.

the hollandite structure,  $Ti_2O_3$ , and either nickel oxide (NiO) or Ni metal nanocrystals.

#### ACKNOWLEDGMENTS

This work was supported by ther Federal Target Program "Scientific and Educational Cadres of the Innovation Russia" of 2009–2013, part "Development of Membranes and Catalytic System" (State Contract no. P869).

#### REFERENCES

- 1. A. Corma, Chem. Rev. 97, 2373 (1997).
- G. J. De, A. A. Soler-Illia, C. Sanchez, et al., Chem. Rev. 102, 4093 (2002).
- D. E. De Vos, M. Dams, B. F. Sels, et al., Chem. Rev. 102, 3615 (2002).

- T. W. Kim, S.-J. Hwang, S. H. Jhung, et al., Adv. Mater. 20, 539 (2008).
- 5. T. W. Kim, S. G. Hur, and S.-J. Hwang, Adv. Funct. Mater. 17, 307 (2007).
- T. W. Kim, H.-W. Ha, M.-J. Paek, et al., J. Phys. Chem. 112, 14853 (2008).
- H. M. Park, T. W. Kim, S.-J. Hwang, et al., Bull. Kor. Chem. Soc. 27, 1323 (2006).
- S. Chen, S. Zhang, W. Liu, et al., J. Hazard Mater. 155, 320 (2008).
- 9. Jr. C. F. Baes and R. E. Mesmer, *The Hydrolysis of Cations* (Wiley, New York, 1982).
- 10. T. W. Kim, I. Y. Kim, J. H. Im, et al., J. Photochem. Photobiol. A: Chem. **205**, 173 (2009).
- 11. R. Khan and T.-J. Kim, J. Hazard. Mater. **163**, 1179 (2009).
- 12. S. Debnath and U. C. Ghosh, Chem. Eng. J. **152** (2–3), 480 (2008).
- 13. L. M. Nunes, V. A. de Cardoso, and C. Airoldi, Mater. Res. Bull. **41** (6), 1089 (2006).
- L. M. Nunes, V. A. de Cardoso, and C. Airoldi, Mater. Res. Bull. 41 (6), 1089.
- T. Sanchez-Monjaras, A. V. Gorokhovsky, and J. I. Escalante-Garcia, J. Am. Ceram. Soc. 91 (9), 3058 (2008).
- M. A. Aguilar González, A. Gorokhovsky, A. Aguilar Elquezabal, J. I. Escalante Garcia, Bol. Soc. Esp. Ceram. 47 (1), 29 (2008).
- 17. T. Nakato, H. Edakubo, and T. Shimomura, Micropor. Mesopor. Mater. **123**, 280 (2008).
- L. A. Bursill and B. G. Hyde, Philos. Mag. 23 (181), 3 (1971).
- K. Yu. Ponomareva and I. D. Kosobudskii, Proceedings of the 7th Scientific Conference "Solid State Chemistry and Advanced Micro- and Nanotechnologies" (Kislovodsk (Russia), 2007), p. 203.