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Layered titanates in alkaline, acidic and intercalated with 1,8-octyldiamine forms as ion-exchangers with divalent cobalt, nickel and copper cations

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Abstract

The precursor crystalline alkaline titanate $K_2Ti_4O_9$ had the potassium ion-exchanged with an acidic solution to yield $H_2Ti_4O_9$, which was intercalated with 1,8-octyldiamine inside the interlayer nanospace to give Oct-$H_2Ti_4O_9$. These three matrices were exchanged with divalent cobalt, nickel and copper cations at the solid/liquid interface and it was verified that as a general behavior, the matrix $K_2Ti_4O_9$ have the highest ion-exchange capacity towards the chosen metallic cations, when compared with the other matrices. The carbon and hydrogen elemental analyses demonstrated a decrease in the amount of diamine after ion exchange process, reflecting the successive displacement of the inserted organic molecule in the inorganic matrix with the progress of the exchanging reaction. The amount of divalent cations exchanged for those three matrices follow the order: Cu > Co > Ni.

Keywords: A. Layered compounds; A. Oxides; B. Intercalation reactions

1. Introduction

The class of nanomaterials formed by layered oxides containing quadrivalent metals is often employed in the removal/separation of several radio/bio-toxic metal ions from aqueous solutions, since they are quite effective for cation as well as for anion separations. When those compounds act as cation-exchanger materials in alkaline solutions, the effectiveness depends upon the basicity of the central atom and the strength of the M–O bond relative to that of the O–H bond in the hydroxyl group [1] and the in acidic solutions is restricted by the facility in retaining protons [2,3]. The resulting compound maintains the original layered structure, which is similar to that one of the alkaline exchangers. Acidic-layered oxide is commonly named as layered hydrous titanium dioxide and exhibits distinct intercalation behaviors towards several cations and some organic compounds [4–6].

To benefit the structural features of these nanocompounds as a synthetic source for cation-exchanging process can be useful mainly due to the presence of various heavy metal toxic ions in the environment, as a consequence of recent high degree of industrialization/urbanization [7]. Thus, these polluting ions in the biological environment constitute a

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serious problem related to the degradation of human health. The ion exchange properties can be explored to removal or immobilize heavy toxic metal ions Cr(VI), radioactive nuclides ^{137}Cs and ^{90}Sr from high-level liquid waters [8,9], to study ion exchange reaction rates of mixed aqueous solution of monovalent alkaline chlorides and hydroxide as function of pH [8,10].

The aim of this investigation is to follow the ion-exchange titanate matrix capacities in alkali ($K_2Ti_4O_9$) or acidic ($H_2Ti_4O_9$) forms, and also the 1,8-octyldiamine intercalated compound (Oct-$H_2Ti_4O_9$) with divalent cobalt, nickel and copper cations in aqueous solution.

2. Experimental

All chemicals used: TiO_2, K_2CO_3, 1,8-octyldiamine, divalent cobalt, nickel and copper acetates were of analytical grade and were employed without further purification. The layered potassium tetratitanate ($K_2Ti_4O_9$) was prepared by solid-state reaction through the heating of stoichiometric mixture of K_2CO_3 and TiO_2 powders in a platinium crucible at 1073 K for 20 h. The obtained solid was grounded and heated again at the same temperature for a further 20 h [10].

The acidic matrix ($H_2Ti_4O_9$) was prepared by suspending the precursor alkaline matrix in hydrochloric acid solution. In a typical experiment, 1.0 g of matrix was suspended under stirring with 20.0 cm^3 of 1.0 mol dm^{-3} solution for 3 days at 343 K. The solid was separated by centrifugation, washed extensively with doubly distilled water until the filtrated solution presented a pH in the range 5.0–6.0. The final obtained product was dried over a saturated sodium chloride solution, to give 70% of relative humidity and was then characterized.

The intercalated compound was prepared by suspending 4.0 g of acidic matrix in 125.0 cm^3 of 0.30 mol dm^{-3} of an 1,8-octyldiamine ($C_8H_{20}N_2$) aqueous solution and the suspension was mechanically stirred for 8 days at 298 ± 1 K. After this time, the solid was separated by centrifugation, washed with doubly distilled water and dried at 303 K. The amount of inserted amine into the lamella was determined by elemental analyses.

The ion-exchange process was performed by suspending 0.50 g of any matrices in 50.0 cm^3 of 0.15 mol dm^{-3} divalent acetate aqueous solutions, which samples were mechanically stirred for 6 h at 298 ± 1 K. After this time, the solid was separated by centrifugation and washed with doubly distilled water up to pH 5.0–6.0 and dried at 313 K for 24 h. The pH of the solution was measured before and after the exchange process did not present a significant difference.

The amount of the exchangeable cations in solution was determined by complexometric titration with a 0.020 mol dm^{-3} EDTA solution [11]. The number of cations exchanged (n_f) was determined through the relationship: $(n_i - n_s)/m$, where n_i is the initial number of moles of cations in solution, n_s the number of moles of cations in equilibrium at the solid/liquid interface after the exchange process and m is the mass of the exchanger used in each operation.

All matrices were characterized before and after the ion-exchange process by using: (i) X-ray diffraction by employing Cu Kα in the 2θ range from 3° to 50° on a Siemens diffractometer model D5000, (ii) thermogravimetry through a Shimadzu TGA-50 instrument by heating samples of about 5.0 mg, from 25 to 950 °C, with a heating rate of 0.17 K s^{-1}, under nitrogen atmosphere, (iii) CHN elemental analysis was carried out with a Perkin-Elmer PE-2400 analyzer and (iv) infrared spectroscopy was performed on a Bomem apparatus, using KBr discs in the 4000–400 cm^{-1} range, with a resolution of 4.0 cm^{-1}.

3. Results and discussion

3.1. Octyldiamine intercalation

The synthesized precursor layered titanate $K_2Ti_4O_9$ is constituted by TiO_6 octaedra units sharing edges at one level that combine with similar units above and below, to form zigzag strings of octaedra [10]. The charge balance is maintained by the occupancy of the alkali metal ions between the layers, as shown in Fig. 1. The free available nanospace inside the layers can be used to insert a guest molecule, however, a more appropriated condition is favorable when the acidic crystalline lamellar compound $H_2Ti_4O_9$ can be employed as host for intercalating the chosen 1,8-octyldiamine molecules. This process can be interpreted as a neutralization of the basic amino center of the organic polar molecule by the acidic center disposed into the lamellar cavity, in a typical Brönsted acid–base reaction [12]. After this previous amine intercalation with long aliphatic chain causes enough expansion to favor divalent cation