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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Sorption of Phosphate Ions with Materials Based on Titanium and Lanthanum Hydroxides

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Abstract—The possibility of preparing lanthanum(III) hydroxide and a 1:1 mixture of lanthanum(III) hydroxide with hydrated titania by precipitation from aqueous solutions was explored. The maximal sorption capacities of the mixture with respect to phosphate ions in acid and alkaline media were determined. The mechanism by which phosphates are removed was elucidated by IR spectroscopy.

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When getting into water basins with domestic and process wastewater and fertilizers washed out from soils, phosphorus compounds stimulate growth of blue-green algae whose rotting products in water include hydrogen sulfide, mercaptans, phenols, and other toxic compounds [1]. When accumulated in human and animal bodies, phosphates cause hyperphosphatemia. Synthetic ion exchangers based on hydrated oxides of III–IV group metals (primarily titanium, iron, and aluminum) were suggested for removal of phosphate ions from water [2–6]. Of special current interest is a development of sorbents for removing phosphates from the gastrointestinal tract. In this context, much promise is offered by lanthanum carbonates and oxycarbonates synthesized from solutions [7, 8], as well as systems based on titanium and lanthanum oxides obtained by spray drying [9].

Hydrated titania not only possesses high sorption capacity but also is highly suitable as sorbing agents carrier [10–12].

Here, we examined sorption of phosphate ions on lanthanum(III) hydroxide and lanthanum(III) hydroxide–hydrated titania mixture obtained by precipitation from aqueous solutions.

EXPERIMENTAL

Lanthanum(III) hydroxide **I** and a 1:1 lanthanum(III) hydroxide–hydrated titania mixture **II** were precipitated from 1 M solutions of lanthanum nitrate and titanium chloride with 3 M ammonia. The resulting materials were washed with distilled water till neutral pH was achieved and air-dried at room temperature.

The X-ray examinations were carried out on a X'Pert Pro PW 3040 Philips diffractometer with CuK_α radiation (λ = 15418 nm). The electron images of the samples were obtained with JEOL JSM-35SF scanning electron microscope. The pore radius distribution was determined on a Quantachrome NOVA 2200 instrument by nitrogen adsorption-desorption method. The IR spectra (KBr pellets) were recorded on a Specord M-80 instrument. The pH-potentiometric measurements were carried out on an I-160M instrument using NaOH and HNO_3 solutions against the background of 0.1 M sodium nitrate. Sorption of phosphate ions was examined under static conditions in $Na_2HPO_4 \cdot 2H_2O$ solutions acidified with nitric acid, if necessary. The sorbent (200 mg) was added to 20 ml of the solution, and the system was equilibrated under shaking for 4 h. The mixture was left to stand for 72 h, after which the

Static sorption capacity A of hydrated titania, lanthanum hydroxide, and their mixture with respect to phosphate ion (c_0 = 52 mM)

Sample	pH_{in}	pH_{eq}	A, mmol g^{-1}
Hydrated titania	8.67	8.71	0.7
	6.96	7.07	1.0
	2.83	4.08	1.6
Lanthanum(III) hydroxide	9.12	11.71	2.0
	7.20	9.77	2.6
	2.46	6.72	4.15
Lanthanum(III) hydroxide–hydrated titania mixture	9.31	10.72	1.6
	7.21	9.35	2.1
	2.34	6.88	4.10

precipitate was filtered off, and the content of phosphate ions in the filtrates was determined photocolorimetrically on a KFK-2 instrument in the form of vanadium phosphomolybdate complex. The sorption capacity A, mmol g^{-1}, was calculated by the formula

$$A = 10^{-3}(c_0 - c_{eq})V/m,$$

where c_0 and c_{eq} are the sorbate concentrations in the initial and equilibrium solutions after sorption, respectively, M; V, volume of solution, ml; and m, sorbent mass, g.

The synthesized materials have different structures. According to X-ray diffraction data, hydroxide **I** is a crystalline compound containing $La_2O(CO_3)_2{\cdot}xH_2O$ impurity (Fig. 1a), and mixture **II** is X-ray amorphous, by contrast (Fig. 1b). The scanning electron microscopic examinations showed that the particle size of individual lanthanum(III) hydroxide widely varies (Fig. 2a), and mixture **II** consists of nearly spherical aggregates measuring < 100 nm in diameter (Fig. 2b). The above-said suggests that individual lanthanum hydroxide **I** has no pronounced pore structure, and mixture **II** is characterized by mesoporous structure with the predominant pore radius of ca. 2.8 nm (Fig. 3).

The ion-exchange characteristics of mixture **II** were determined by pH-potentiometric examinations which showed that the mixture is a typical ampholyte (Fig. 4). Its ion-exchange capacity in acid and alkaline media was estimated at 6 and 2.25 mmol g^{-1}, respectively.

Table lists the results of comparative examination of sorption of phosphate ions (c_0 = 52 mM) on hydrated titania, lanthanum(III) hydroxide, and their mixture. All the three materials perform much better in phosphate ion removal in acid media. Both in acid and alkaline media sorption of phosphate ions is accompanied by an increase in pH of medium, most likely due to anion exchange involving hydroxy groups. Moreover, in alkaline media anion exchange should be paralleled by cation-exchange sorption of sodium ions, which also affects pH. Hydrated titania performs poorer in phosphate absorption than hydroxide **I** and mixture **II**, whose sorption capacities are very close. Since titanium and lanthanum hydroxides differ in the precipitation pH (1.5–2 against

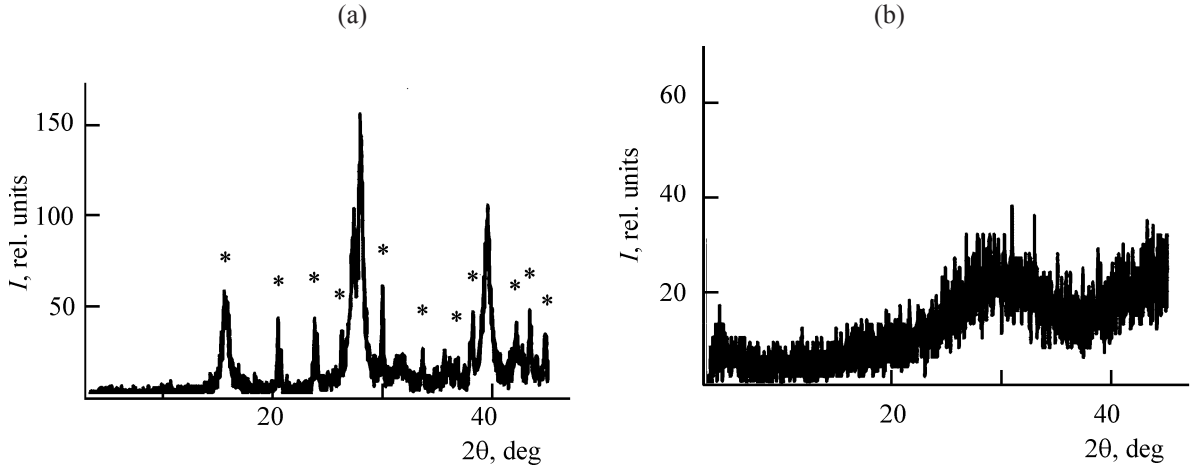

Fig. 1. X-ray diffraction patterns of (a) individual hydroxide **I** and (b) mixture **II**. (I) Intensity, and (2θ) Bragg's angle. Asterisks mark peaks belonging to $La_2O(CO_3)_2{\cdot}xH_2O$ (JCPDS 28-0512); unmarked peaks belong to $La(OH)_3$ (JCPDS 36-1481).

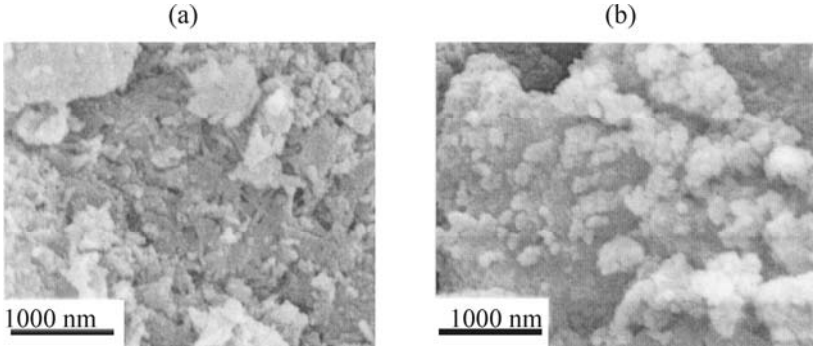

Fig. 2. Electron images of (a) individual hydroxide **I** and (b) mixture **II** (×30 000 magnification).

8.5 [13]), it can be presumed that, during precipitation, the surface of hydrated titania gets coated with a lanthanum hydroxide layer. Considering high cost of lanthanum-containing raw material, this makes binary mixtures promising for sorption applications.

Figure 5 presents the isotherms of sorption of phosphate ions on mixture **II**. They do not reach saturation, which is typical for amorphous materials having multiple sorption sites [12]. The maximal sorption capacity in acid media (pH 2.3–2.6) was estimated at 5.5 mmol g^{-1}, and in alkaline media (pH 9.1–9.3), at 3.35 mmol g^{-1}. At low concentrations (1–5 mM) virtually 100% of phosphate ions is removed.

The sorption mechanism for phosphate ions was elucidated by IR spectroscopy. Figure 6a shows the IR absorption spectra of individual lanthanum hydroxide **I**, and Fig. 6b, those of mixture **II** in the region corresponding to vibrations of phosphate ions (800–1300 cm^{-1}), carbonate ions (1200–1800 cm^{-1}), and hydroxy groups (1700–4000 cm^{-1}) before and after sorption. The regions of vibrations in Fig. 6 were assigned irrespective of the degree of protonation of the anions.

A feature specific of the spectrum of hydroxide I (Fig. 6a, curve *1*) is a line at ν = 3610 the cm^{-1}, corresponding to vibrations of hydroxy groups of the crystal, not involved in hydrogen bonding [14–16]. This line is lacking in the spectrum of the mixture (Fig. 6b, curve *1*), which is probably another evidence in favor of the amorphous nature of mixed hydroxide.

As mentioned above, sorption of phosphate ions is accompanied by an increase in pH of medium due to anion exchange involving hydroxy groups, as manifested in the IR spectra. For example, upon sorption of phosphates on $La(OH)_3$ both from acid and alkaline solutions the absorption band at ν = 3610 cm^{-1}

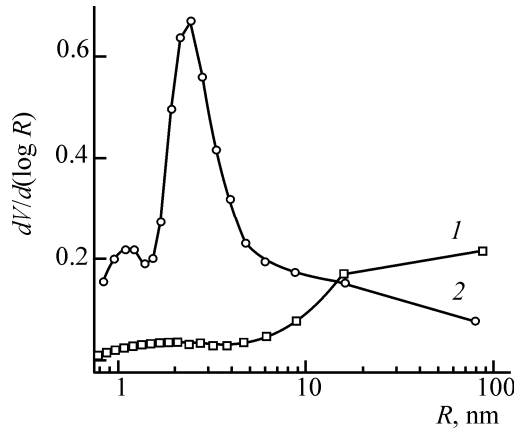

Fig. 3. Pore radius distribution $dV/d(\log R)$ for (*1*) lanthanum(III) hydroxide and (*2*) lanthanum(III) hydroxide–hydrated titania mixture. (*R*) Pore radius.

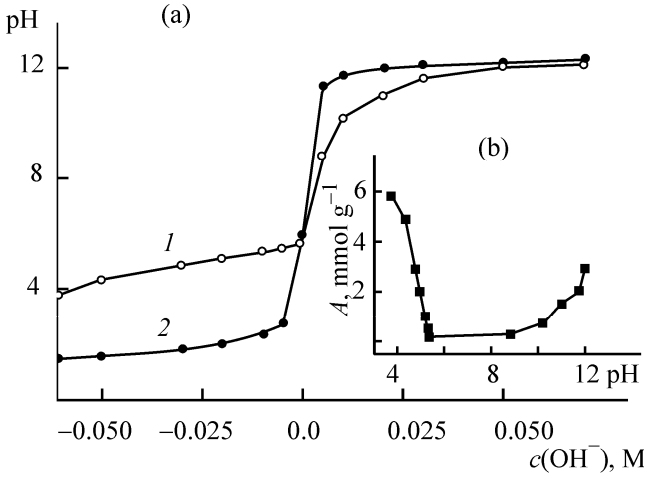

Fig. 4. Variation of (a) pH of HNO_3 and NaOH solutions against background of 0.1 M $NaNO_3$ (*1*) with and (*2*) without lanthanum(III) hydroxide–hydrated titania mixture and (b) sorption capacity *A* vs. pH.

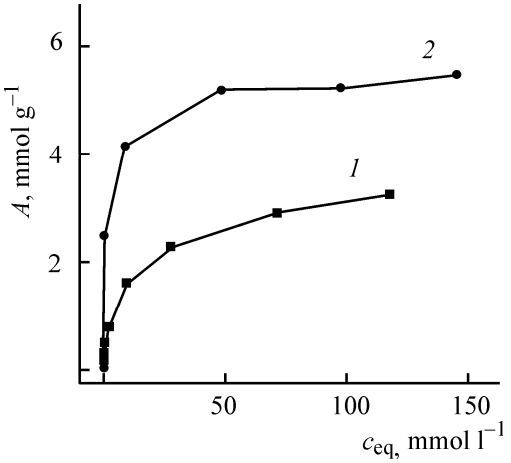

Fig. 5. Isotherms of sorption of phosphate ions with mixture **II**. (*A*) Sorption capacity and (c_{eq}) concentration of phosphate ions in the equilibrium solution after sorption. pH of solution: (*1*) 2.3–2.6 and (*2*) 9.1–9.3.

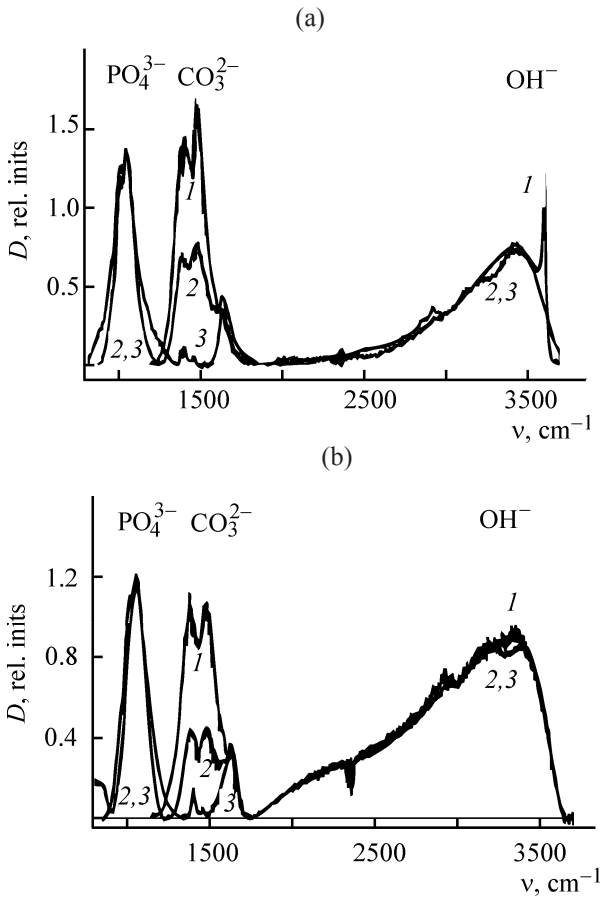

Fig. 6. IR absorption spectra of (a) individual hydroxide **I** and (b) mixture **II** (*1*) before and (*2, 3*) after sorption of phosphate ions from solutions with pH of (*2*) 9.1–9.3 and (*3*) 2.3–2.5. (*D*) Optical density and (ν) wave number.

characteristic only for this sorbent disappears (Fig. 6a). The removal of phosphates with mixture **II** is accompanied by a change in intensity of the absorption band of hydroxy groups near 3250 cm^{-1}, whatever pH of solution (Fig. 6b).

Lastly, the IR absorption spectra suggest that the sorption of phosphate ions with lanthanum-containing materials involves replacement of carbonate ions. In alkaline solutions (Figs. 6a, 6b, curves *2*) the phosphate ions replace approximately 50% of the available carbonate. In acid solutions (Figs. 6a, 6b, curves *3*) virtually 100% of carbonate is removed from the sorbent.

CONCLUSIONS

(1) Precipitation with ammonia from aqueous solutions of titanium chloride and lanthanum nitrate, taken in a 1:1 ratio, yields an X-ray amorphous, nanosize (particle size under 100 nm), mesoporous (pore radius ca. 2.8 nm) mixture of lanthanum(III) hydroxide and hydrated titania. Lanthanum(III) hydroxide containing $La_2O(CO_3)_2{\cdot}xH_2O$ impurity is precipitated in the crystalline state and exhibits no pronounced pore structure.

(2) The maximal sorption capacity of the lanthanum(III) hydroxide–hydrated titania mixture with respect to phosphate ions was estimated at 5.5 and 3.35 mmol g^{-1} for acid and alkaline media, respectively.

(3) An IR spectroscopic examination showed that the removal of phosphates from aqueous solutions with lanthanum-containing materials is underlain by anion exchange involving hydroxy groups and is associated with replacement of carbonate ions from the sorbents.

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REFERENCES

1. Ashirov, A., *Ionoobmennaya ochistka stochnykh vod, rastvorov i gazov* (Ion-Exchange Treatment of Wastewater, Solutions, and Gases), Leningrad: Khimiya, 1983.

2. Evdokimova, L.I., Boichinova, E.S., Timofeeva, V.N., and Brynzova, E.D., *Zh. Prikl. Khim*., 1979, vol. 52, no. 6., p. 1409.
3. Laiti, E., Persson, P., and Oeman, L.-O., *Langmuir*, 1998, vol. 14, p. 825.
4. Michelmore, A., Cong, W., Jenkins, P., and Ralston, J., *Phys. Chem. Chem. Phys*., 2000, vol. 2, p. 2985.
5. Romanova, I.V., Lozovskii, A.V., and Strelko, V.V., *Khim. Technol. Vody*., 2005, vol. 27, p. 313.
6. Zykova, O.P., Khodakovskaya, T.A., Markiv, E.Ya., et al., *Zh. Prikl. Khim*., 2007, vol. 80, p. 1811.
7. US Patent 20060134225.
8. US Patent 20080069860.
9. EEC Patent EP1328468
10. Pendelyuk, O.I., Lisnycha, T.V., Strelko, V.V., and Kirillov, S.A., *Adsorption*, 2005, vol. 11, p. 784.
11. Pendelyuk, O.I., Lesnichaya, T.V., and Kirillov, S.A., *Dop. Nats. Akad. Nauk Ukraini*, 2006, no. 10, p. 195.
12. Kirillov, S.A., Lisnycha, T.V., and Pendelyuk, O.I., *Separ. Sci. Tech*., 2006, vol. 24, p. 895.
13. Aksel'rud, R.V., *Usp. Khim*., 1963. vol. 22, p. 812.
14. Balicheva, T.G. and Lobanova, O.A., *Elektronnye i kolebatel'nye spektry neorganicheskikh i koordinatsionnykh soedinenii* (Electronic and Vibrational Spectra of Inorganic and Coordination Compounds), Leningrad: Len. Gos. Univ., 1983.
15. Klevtsov, P.V., Klevtsova, R.F., and Sheina, L.P., *Zh. Struk. Khim*., 1967, vol. 8, p. 268.
16. Atoji, M. and Williams, D.E., *J. Chem. Phys.,* 1959, vol. 31, p. 329.