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ZIRCONIUM (IV) OXIDE AS PERSPECTIVE SORBENT OF IONS FROM AQUEOUS SOLUTIONS

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Progress in the field of inorganic sorbents is associated with the search for new materials and improvement of existing ones. When used, a number of requirements are imposed on them, namely: cheapness, ease of preparation, reusability, high efficiency and selectivity. Among these requirements, the cheapness (allows to obtain sorbents of the lowest cost and therefore with high economic efficiency) and high selectivity (obtaining sorbent materials that can provide purification of aqueous solutions from pollutants of a certain nature, i.e. sorbents of a certain targeted action) deserve the most attention.

One of the materials capable of selective sorption of many ions is zirconium (IV) oxide, which is effective in wastewater treatment from chlorides, phosphates, sulfates, arsenates, heavy metal ions, etc. However, a significant obstacle to the widespread use of ZrO_2 as a sorbent is, among other things, its relatively high cost. To overcome the latter drawback, it is advisable to develop the direction of creating functional sorption composite materials based on ZrO_2 with a reasonable choice of carrier, which would also have sorption properties. From this point of view, the most promising carriers are natural materials that are available in sufficient quantities in the earth's crust, and therefore can be used with high economic efficiency. One of such promising natural sorption materials is activated carbon due to its developed surface, widespread availability and low cost. Even more promising is the combination of activated carbon with various expensive sorbents, such as nanodispersed zirconium (IV) oxide, which will contribute to a significant increase in both the specific surface area of the latter and the reactivity of zirconium (IV) oxide.

Thus, the combination of nanoscale zirconium (IV) oxide and activated carbon should have a positive effect on the sorption characteristics of the future composite sorbent, and, expectedly, on the technical and economic feasibility of its use in terms of complex indicators. *Key words:* zirconium oxide, sorption, activated carbon, composite, heavy metal ions, wastewater.

Цирконію (IV) оксид як перспективний сорбент йонів із водних розчинів. Феденко Ю.М., Самойленко В.О.

Прогрес у галузі неорганічних сорбентів пов'язаний з пошуком нових матеріалів та вдосконаленням існуючих. При застосуванні до них пред'являється ряд вимог, а саме: дешевизна, простота одержання, можливість повторного застосування, висока ефективність та селективність. Серед цих вимог найбільшої уваги заслуговують саме дешевизна (дозволяє отримувати сорбенти найнижчої вартості і тому з високою економічною ефективністю) та висока селективність (одержання сорбційних матеріалів, що здатні забезпечувати очищення водних розчинів від забрудників певної природи, тобто сорбенти певної цілеспрямованої дії).

Одним з матеріалів, що здатен до селективної сорбції багатьох йонів, є цирконію (IV) оксид, який є ефективним при очищенні стічних вод від хлоридів, фосфатів, сульфатів, арсенатів, йонів важких металів тощо. Проте, суттєвою перешкодою для широкого використання ZrO_2 як сорбента є, серед іншого, його відносно висока вартість. Для подолання останнього недоліку доцільно розвивати напрямок створення функціональних сорбційних композиційних матеріалів на основі ZrO_2 з обґрунтованим вибором носія, котрий теж володів би сорбційними властивостями. З цієї точки зору найбільш перспективними носіями представляються природні матеріали, які в достатній кількості наявні в земній корі, а тому можуть бути використані з високою економічною ефективністю. Одним із таких перспективних природних сорбційних матеріалів є активоване вугілля завдяки його розвиненій поверхні, розповсюдженості та невисокій вартості. Ще більш перспективним виглядає поєднання активованого вугілля з різними дороговартісними сорбентами, як, наприклад, нанодисперсним цирконію (IV) оксидом, що сприятиме значному зростанню як питомої площі поверхні останнього, так і реакційної здатності цирконію (IV) оксиду.

Отже, поєднання нанорозмірного цирконію (IV) оксиду та активованого вугілля повинно позитивним чином вплинути як на сорбційні характеристики майбутнього композиційного сорбента, так і, очікувано, на техніко-економічну доцільність його використання за комплексними показниками. *Ключові слова:* цирконію оксид, сорбція, активоване вугілля, композит, йони важких металів, стічна вода

Introduction. Crystalline zirconium (IV) oxide (ZrO_2) can exist in monoclinic (thermodynamically stable up to a temperature of 1170 °C), tetragonal (stable from 1170 °C to 2370 °C) and cubic (stable from 2370 °C to the decomposition temperature of the compound – 2700 °C) modifications [1].

Cubic ZrO_2 has the structure of fluorite, in the crystal lattice of which each Zr atom has eight bonds with Oxygen atoms. Thus, Zr atoms form centrosymmetric lattice with axis translation (CSL) with Oxygen atoms occupying positions in tetrahedral interstices. The cubic structure is determined by one lattice constant (Table 1) [2–4].

Tetragonal ZrO_2 can be considered as a slightly distorted cubic structure. The structure of tetragonal ZrO_2 is defined by two lattice parameters – a and c. In the crystalline tetragonal structure of ZrO_2, Zr atoms are also bonded to eight Oxygen atoms – four adjacent Oxygen atoms are located in the plane of the tetrahedron; the length of the Zr-O bond is 0.207 nm, and the remaining Oxygen atoms are located at an angle of 90 ° to the plane of the tetrahedron at a distance of 0.246 nm from Zr [2-4].

Monoclinic ZrO_2 is formed by further distortion of the tetragonal structure. It is even less symmetrical and is represented by more complex geometric structures of 12 atoms of the unit cell. In monoclinic ZrO_2, Zr atoms have seven bonds with Oxygen (Fig. 1). In space, the Oxygen atoms form angles of 134.5° and 109.5°. Thus, the Oxygen atoms are not in the same plane. In the crystal structure of monoclinic ZrO_2, the interatomic distances of Zr-O vary significantly, but have an average value of 0.207 nm and 0.221 nm [2–4].

Fig. 1 shows polymorphic modifications of ZrO_2 – their atomic structures and corresponding unit cells.

The transition to the monoclinic phase during cooling occurs from 1000 °C to 650 °C. On the other hand, during heating, the monoclinic phase transforms into the tetragonal phase starting from 820 °C. In this case, the tetragonal modification is formed even up to 1170 °C [5].

Tetragonal modification of ZrO_2 is unstable. To stabilize it, so-called tolerance agents (usually oxides of rare earth metals, calcium, magnesium, ferrum) are used. Ceramic material based on zirconium (IV) oxide stabilized with yttrium oxide (Y-TZP – Yttrium-Tetragonal Zirconia Polycrystal) is promising for use in restorative dentistry [7–13].

Applications of nanomaterials based on zirconium (IV) oxide. As mentioned above, modifications of nanodispersed ZrO_2 in nanomaterials based on it determine the ways of application, because each of its modifications has a number of unique properties.

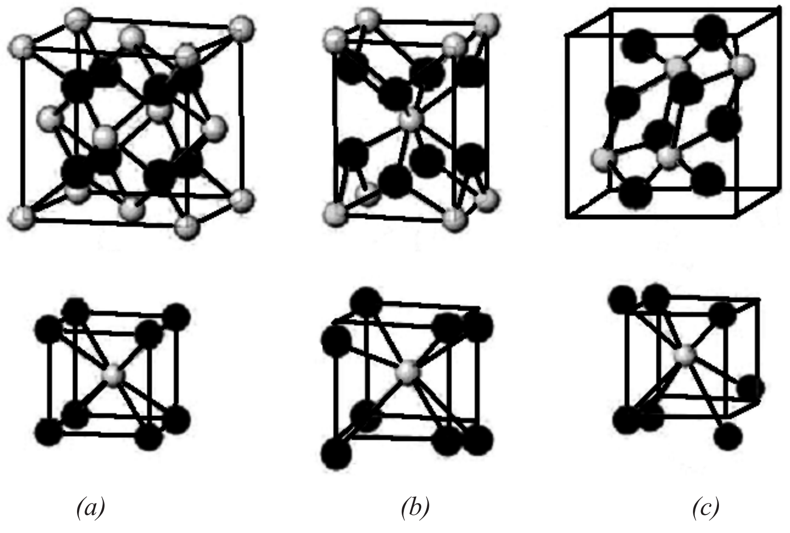
ZrO_2 crystalline powders of monoclinic modification have catalytic properties, and cubic and tetragonal modifications – high strength and thermal stability. In addition, the cubic modification of ZrO_2 has ionic conductivity, which leads to its use in such a promising direction as the production of solid oxide fuel cells.

Therefore, the monoclinic modification of ZrO_2 nanopowder is used mainly in the production of substrates for luminescent and photosensitive materials [14], and nanomaterials based on ZrO_2 of tetragonal and cubic modifications – in ceramic materials, including, in new materials with a set of enhanced service characteristics

Table 1

Parameters of ZrO_2 crystal lattice and some of its characteristics [1–5]

Phase	Simple group	Lattice parameters	Bulk density, g/cm^3	Band gap width, eV	Temperature stability
Monoclinic	P 2_1/c	*a*=0,5169 nm, *b*=0,5232 nm, *c*=0,5341 nm, β=99˚15’ (20 ˚C)	5,6	5,83	up to 1170 ˚C
Tetragonal	P 4_2/nmc	*a*=0,514 nm, *b*=0,527 nm, *a/c*=1,02 (1250 ˚C)	6,1	5,78	1170-2370 ˚C
Cubic	Fm/3m	*a*=0,5256 nm (2330 ˚C)	6,27	6,1	2370-2700 ˚C



(a) (b) (c)

Fig. 1. Atomic structures (top) and coordinated relative to each other Oxygen (black) and Zirconium (white) atoms of unit cells (bottom) of different modifications of ZrO_2: (a) – cubic, (b) – tetragonal, (c) – monoclinic

due to increased viscosity, high mechanical, radiation and corrosion resistance, hardness, melting point, refractoriness, satisfactory electrical conductivity and low thermal conductivity at low temperatures [14]. Hence, the tetragonal modification of zirconia (IV) oxide has been widely used as a bio-ceramic in restorative dentistry [15], and the cubic modification as a chemical and heat-resistant nanoceramic of high strength [16–18]. In addition, as mentioned above, the cubic modification of zirconia (IV) oxide is used as a solid electrolyte in solid oxide fuel cells and as a protective anti-corrosion coating for steel [19].

In addition, zirconium (IV) oxide in the monoclinic modification is used as a catalyst (due to the activity of acid centers on the surface) [20], in the tetragonal modification – as a carrier for catalysts (due to high thermal stability) [21], as a sorbent in the amorphous phase or at a low degree of crystallinity [22].

When using zirconium (IV) oxide as a catalyst, an important role is played by the acid-base nature of its properties and the presence of several types of defects in the crystal lattice and on the surface, which are one of the main factors of the reaction-catalytic activity of the surface of any oxide. When obtaining these oxides in the form of nanostructures, the percentage of coordination-unsaturated ions, especially at the edges and corners of microcrystallites, is predicted to be large. Consequently, the physical chemistry of the surface in nanoscale systems based on metal oxides will play a crucial role in determining the scale of their application and evaluation of catalytic activity.

Zirconium (IV) oxide, when used as a carrier for catalysts, must have sufficiently developed external and internal surface areas. These requirements are met by obtaining the smallest possible size of zirconium (IV) oxide crystallites.

One of the most unusual and promising properties of zirconium (IV) oxide particles is its sorption capacity for both anions and cations, which allows us to consider nanoscale ZrO_2 and materials based on it as a tool for improving the ecological state of the environment. At the same time, the greatest sorption capacity has hydrated zirconium (IV) oxide, i.e. in the amorphous state [23-25]. The peculiarity of the use of ZrO_2 as a sorbent is that it has a high selectivity for multivalent anions (chromates, borates, sulfates, phosphates, arsenates, etc.) and can be used at high temperatures without losing its efficiency.

Thus, it can be argued that ZrO_2 is a multifaceted material that has many real and promising applications. Due to this, it attracts increased interest, and in the transition to nanostructures it has numerous advantages for obtaining new types of materials with improved characteristics, among which the least studied are sorption properties.

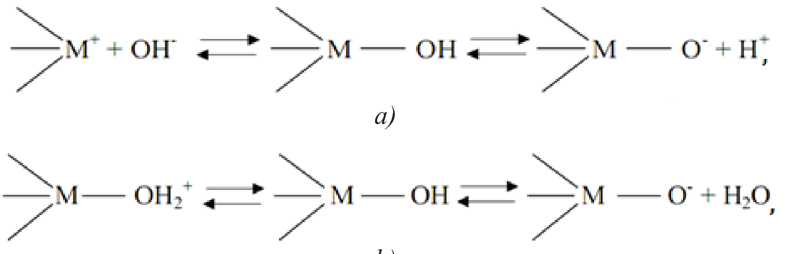
Application of nanosized zirconium (IV) oxide and composites based on it as sorbents. Zirconium (IV) oxide in the amorphous state, due to the developed surface and the presence of hydroxide groups, can be effectively used as a sorbent for both anions and cations depending on the pH (due to the amphoteric properties of zirconyl cation). The active surface of hydrated zirconium (IV) oxide, depending on the pH of solutions, is formed by two mechanisms [23] (Fig. 2).

Based on the above mechanisms, in this type of sorbents, in particular ZrO_2, there is a transition from sorption of anions in an acidic environment to cations in an alkaline one. The transition from one type of sorption to another corresponds to the achievement of the isoelectric point of the Zirconium ion, which is equal to pH 4 [21].

In [22], the sorption of both anions (Cl-, $H_2PO_4^-$, SO_4^{2-}, etc.) and cations (Na^+, As^{3+}, Sr^{2+}, etc.) on ZrO_2 nanopowders was studied. It was shown that anions were removed more efficiently at pH less than 5, and cations – at pH more than 8.

Sorption of zirconium (IV) oxide occurs due to surface hydroxide groups. Water contained in ZrO_2, according to [23], is not hydrated, because it is gradually lost when heated in a certain temperature range, which indicates the non-isobaric nature of dehydration, which is inherent in hydrated compounds. The final amount of water in ZrO_2 powder depends on the final temperature treatment and on the conditions of its synthesis. Thus, in the process of sol-gel synthesis or chemical precipitation during hydrolysis and polymerization, a mesh structure is formed with – O – Zr – O – bridges that have cross-links with Zirconium atoms.

From the data on the study of dehydration and thermogravimetry, which were obtained in [25], it was found



a)

b)

Fig. 2. Formation of the active surface of zirconium (IV) oxide depending on the pH of the environment: a) – acidic environment, b) – alkaline environment

that Zr hydroxides do not form hydrates of a certain composition, and when they are deposited, the $ZrOOH^+$ ion forms the periodic structure (Fig. 3).

The exchange capacity of ZrO_2 also depends on the final temperature: it decreases with its increase. It is noted in [23] that the exchange capacity decreases sharply in ZrO_2 powders obtained at temperatures above 300 °C. This coincides with the transition of the tetragonal structure to the monoclinic structure (290 °C) and may be associated with recrystallization into a more compact form.

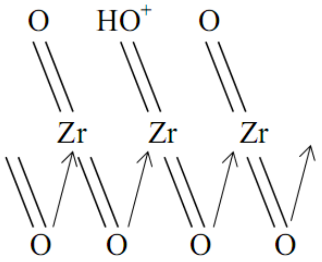


Fig. 3. Periodic structure formed by ion $ZrOOH^+$ deposition

From the above data it follows that hydrated zirconium (IV) oxide is a multifunctional sorbent capable of removing both cations and anions. At the same time, it has high selectivity to some ions [24], which makes it possible to use it in certain cases for the separation of ions in mixtures.

One of the disadvantages of ZrO_2 when used as a sorbent is its relatively high cost. To reduce the cost of such sorbents, composites based on ZrO_2 in combination with various carriers can be used. The choice of carrier is dictated by its properties such as developed surface, chemical inertness, sorption properties, etc. [21]. When using composites based on ZrO_2, it is expected that the sorption process will involve the maximum available surface of zirconium (IV) oxide, while in a similar application of purely ZrO_2, a significant part of its surface may remain inaccessible.

The following materials are currently used as carriers for ZrO_2: Al_2O_3, Fe_2O_3, SiO_2, layered graphite, multiwalled carbon nanotubes [21–24]. However, almost nowhere is the use of activated carbon, which has quite significant advantages over other carriers – high specific surface area (from 600 to 1000 m^2/g) and low cost. In addition, it is likely that the use of the carrier can stabilize the size of ZrO_2 in the nanoscale. All this should have a positive effect on the specific surface area in general and on the sorption characteristics in general.

Thus, ZrO_2 can be quite a promising sorbent for the extraction of cations and anions from aqueous solutions, which will solve some of the environmental problems of our time. At the same time, the synthesis of a nanocomposite based on zirconium (IV) oxide will significantly reduce the cost of such a sorbent, while maintaining or improving its sorption characteristics.

References

1. Кондир А.І. Наноматеріалознавство і нанотехнології : навчальний посібник. Львів : Видавництво Львівської політехніки, 2016. 452 с.
2. Munoz-Aguado M.J., Gregorkiewitz M., Larbot A. Sol-gel synthesis of the binary oxide (Zr, Ti) O_2 from the alkoxides and acetic acid in alcoholic medium. *Materials Research Bulletin*. 1992. Vol. 27. № 1. P. 87–97.
3. Sanders W. Basic Principles of Nanotechnology : book. Boca Raton, US : CRC Press, 2018. 194 p.
4. Benerjee S. Phase Transformations / S. Banerjee, P. Mukhopadhyay. Elsevier Ltd, 2007. 801 p.
5. Jin L., Ni L., Yu Q. Theoretical calculations of thermodynamic properties of tetragonal ZrO_2. *Computational Materials Science*. 2012. Vol. 65. P. 170–174.
6. Пугачевський М.А., Заводинський В.Г., Кузьменко А.П. Диспергування діоксиду цирконію імпульсним лазерним випромінюванням. *Журнал технічної фізики*. 2011. Том 81. Вип. 2. С. 98–102.
7. Obal K., Pedzich Z., Brylewski T. Modification of Yttria-doped tetragonal Zirconia Polycrystal ceramics. *International Journal of electrochemical Sciences*. 2012. № 7. P. 6831–6845.
8. Ruff O., Ebert F. Refractory Ceramics: 1, The Forms of Zirconium Dioxide. Z. *Anorg. Allq. Chem*. 2010. № 180(1). P. 19–41.
9. Шилова О.А., Шилов В.В. Наносистеми, наноматеріали, нанотехнології : монографія. Київ : Академперіодика, 2002. 100 с.
10. Верещак В.Г., Нестеренко Н.Г. Процеси стабілізації високотемпературних кристалічних модифікацій діоксиду цирконію. *Питання хімії і хімічної технології*. 2009. № 3. С. 149–154.
11. Piconi C., Maccauro G. Zirconia as a ceramic biomaterial. *Biomaterials*. 1993. № 20. P. 1–25.
12. Галахов А.В., Фоміна Г.А., Ільїчева А.А. Механічні властивості кераміки в системі «ZrO_2 + 12% CeO_2» з додатками CaO, Y_2O_3, Nb_2O_5. *Вогнетриви*. 1994. № 2. С. 7–10.
13. Badwal S.P.S., Bannister M.J., Hannink R.H.J. Science and Technology of Zirconia. *Lancaster. Technomic Publishing Co.* 1993. 880 p.
14. Ren Z., Zhang G., Paul Chen J. Adsorptive removal of arsenic from water by an iron – zirconium binary oxide adsorbent. *Journal of Colloid and Interface Science*. 2011. Vol. 358. P. 230–237.
15. Long F., Gong J., Zeng J. Removal of phosphate from aqueous solution by magnetic Fe – Zr binary oxide. *Chemical Engineering Journal*. 2011. Vol. 171. P. 448–455.
16. Kikuyama S., Miura A., Kikuchi R. SO_x sorption – desorption characteristics by ZrO_2-based mixed oxides. *Applied Catalysis A: General*. 2004. Vol. 259. № 2. P. 191–197.
17. Kikuyama S., Matsukuma I., Kikuchi R. A role of components in Pt – ZrO_2/Al_2O_3 as a sorbent for removal of NO and NO_2. *Applied Catalysis A: General*. 2002. Vol. 226. № 1. P. 23–30.

18. Kikuyama S., Matsukuma I., Takeguchi T. NO_x sorption – desorption mechanism of ZrO_2-based oxide. *Studies in Surface Science and Catalysis*. 2003. Vol. 145. P. 247–6608.
19. Argon P.A., Fuller J.R., Holmes H.F. IR studies of water sorption on ZrO_2 polymorphs. *Journal of Colloid and Interface Science*. 1975. Vol. 52. Issue 3. P. 553–561.
20. Wu S.F., Wang L.L. Improvement of the stability of a ZrO_2-modified Ni-nano-CaO sorption complex catalyst for Re SER hydrogen production. *International Journal of Hydrogen Energy*. 2010. Vol. 35. № 13. P. 6518–6524.
21. Eguchi K., Kondo T., HayashiT. Sorption of nitrogen oxides on MnO_y – ZrO_2 and Pt – ZrO_2 – Al_2O_3. *Applied Catalysis B: Environmental*. 1998. Vol. 16. № 1. P. 69–77.
22. Slimane R., Abbasian J. Regenerable mixed metal oxide sorbents for coal gas desulfurization at moderate temperatures. *Advances in Environmental Research*. 2000. Vol. 4. № 2. P. 147–162.
23. Moskovits M., Ravi B.G., Chaim R. Sintering of bimodal Y_2O_3 – stabilized zirconia powder mixtures with a nanocrystalline component. *Materials*. 1999. Vol.11. № 2. P. 179–185.
24. Li G., Li W., Zhang M. Morphology and hydrodesulfurization activity of Co, Mo sulfide supported on amorphous ZrO_2 nanoparticles combined with Al_2O_3. *Applied Catalysis A: General*. 2004. Vol. 273. P. 233–238.
25. Davies L.E., Bonini N.A. Locatelli S. Characterization and catalytic activity of zirconium dioxide prepared by sol – gel. *Latin American Applied Research*. 2005. № 35. P. 23–28.