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Review

Crystalline Zeolite Layers on the Surface of Titanium Alloys in Biomedical Applications: Current Knowledge and Possible Directions of Development

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Abstract: In this review, the main focus was on the use of zeolites as layers to modify the surface of titanium implants. The article discusses the basic methods for modifying the functional properties of zeolites (e.g., ion exchange) as well as biomedical applications of zeolites (e.g., drug delivery systems and biosensors). The article reviews the surface modifications of titanium alloys prepared so far with the use of various types of zeolites and selected examples are presented. This review shows the significant impact of titanium surface modification with zeolites, as well as their post-synthetic modification on implant properties, for instance, better biocompatibility, faster osseointegration, better cell adhesion, and corrosion resistance properties. The results of the research presented so far in this review show that the modification of titanium with zeolite layers is a very prospective subject, but underdeveloped, as evidenced by a small number of studies on this subject. We have shown that the prepared layers can be continuously improved and used, e.g., as local delivery systems for various active pharmaceutical ingredients (APIs). We hope that the prepared review will help research groups around the world in the preparation of implants modified with zeolites with even better properties and utility applications.

Keywords: zeolites; titanium implants; ion exchange; biomaterials

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1. Zeolites

Zeolites are biocompatible materials belonging to the group of hydrated aluminum silicates with an ordered microporous structure [1]. They have applications in both industry and biomedical science. Examples of industrial applications of zeolites include molecular sieves in water purification, catalysts of various reactions (e.g., methanol to gasoline), and ion exchangers [2–4]. While biomedical applications include biomolecule separation, drug and gene delivery, and construction of biosensors [5,6]. These materials consist of tetrahedrons of the general formula MO_4 where M is Al or Si in natural zeolites. In the synthetic ones, M can stand for instance for Ti, Zr, B, or Ge [5–9]. Currently, the Structure Commission of the International Zeolite Association (IZA-SC) has recognized 247 unique types of zeolite network structures [10]. During the crystallization process, these tetrahedrons combine with each other by means of the oxygen atom, and additionally due to the fact that aluminum and silicon have different valences, a negative charge is created in the crystal lattice. This negative charge is balanced by cations that are not permanently bound in the crystal lattice, which means that they can be exchanged for other cations [11,12]. In the case of naturally occurring zeolites, they are most often Na^+ and K^+, but they can be replaced with any cation, e.g., Zn^{2+} or Ca^{2+} [13]. A characteristic feature of zeolites is their silicon to aluminum-ratio. It affects their chemical and physical properties. Due to their ratio, they can be divided into 3 groups, Si/Al = 1–2 low silica zeolites (e.g., Linde type A, and X or Y type Faujasites), Si/Al = 3–10 medium silica zeolites (Linde type L), and Si/Al = 10–∞ high silica zeolites (e.g., MFI-Mobile five type, zeolite

Beta). Zeolites having low silicon to aluminum ratio have high hydrophilicity and strongly interact with polar particles while zeolites with high silicon to aluminum ratio have greater hydrophobicity and better interact with non-polar substances [14–16]. Additionally, this ratio influences the ion exchange properties of these materials. The smaller this ratio, the zeolite shows better ion exchange properties [17]. It is also possible to synthesize mesoporous zeolites with larger pore sizes, which increase the application possibilities of these materials [18]. Literature reports also indicate the high stability of zeolites in body fluids, which allows them to be used in the biomedical field [19]. Figure 1. shows one of the most common zeolite frameworks used in various applications.

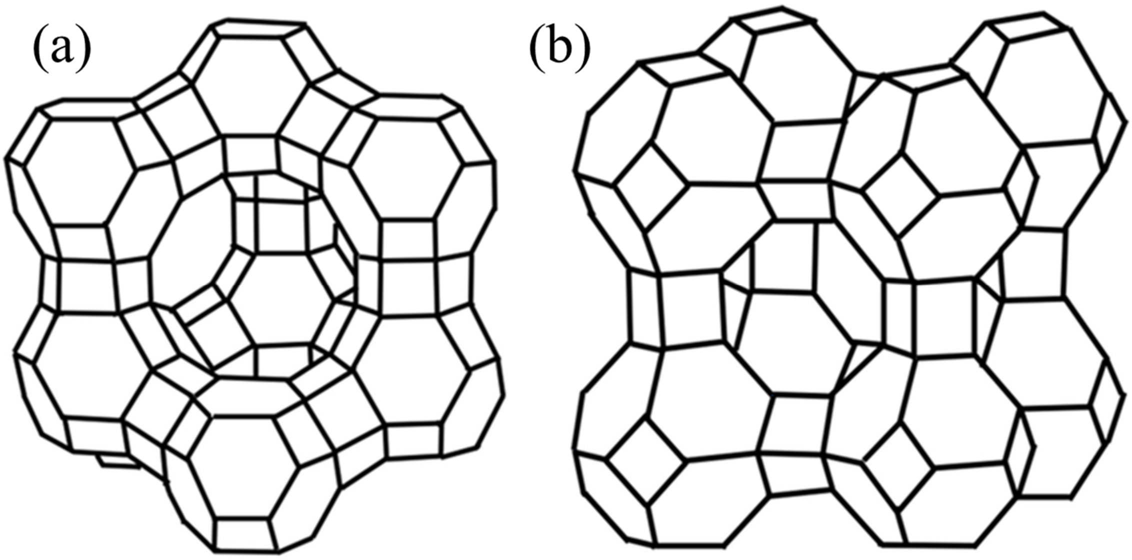

Figure 1. One of the most common zeolite frameworks: (**a**) Faujasite; (**b**) Zeolite type A.

2. Zeolites in Biomaterials

Due to the above-mentioned properties, zeolites have found many biomedical applications. Figure 2 shows some of the most popular biomedical applications of zeolites. For example, many different types of zeolites have been proposed as drug carriers for many drug substances, mainly due to their excellent biocompatibility. Drugs that can be delivered by zeolites are, for instance, curcumin, diclofenac, and cis-platin. Examples of zeolite frameworks used for the administration of these drugs are ZSM-5, NaY, and clinoptilolite [20–23]. Sağir et al. prepared a nanocomposite consisting of magnetite nanoparticles and zeolite 4A. The prepared material was used as the carrier of 5-fluorouracil. The obtained nanocomposites showed superparamagnetic properties and had satisfactory release profiles. The authors also proved that the prepared material has satisfactory anti-cancer properties [24]. One of the recently published papers shows the use of two synthetic forms of faujasite (NaX and NaY) in which the sodium ions have been exchanged for zinc ions (ZnY and ZnX) as a carrier for the anti-cancer drug 6-mercaptopurine. It was proved in this work that zeolites with substituted ions have excellent biocompatibility and good release profiles [25].

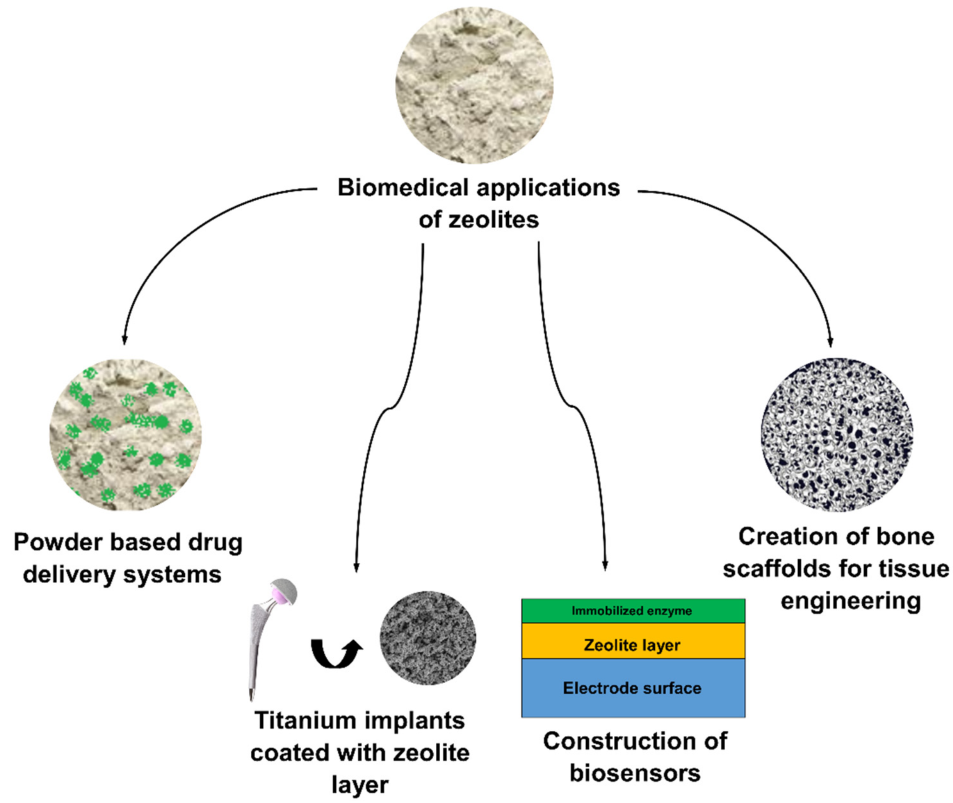

Figure 2. Biomedical applications of zeolites.

Another biomedical application of zeolites is the construction of biosensors. Biosensors are a new group of analytical devices created with the participation of a biological recognition element, which is often, for example, enzyme in close contact with a transducer. Until now, different zeolites have been used to create different types of sensors. The examples of zeolites used for this type of application are zeolite L and β and the enzymes that have been immobilized are e.g., urease or acetylcholinesterase [26,27]. For instance, Kaur and Srivastava prepared a nanocomposite consisting of polyaniline (PANI) and zeolite ZSM-5, on which they immobilized the enzyme—acetylcholinesterase [28]. The obtained biosensor was used for the detection of acetylcholine and organophosphate pesticides. The prepared biosensor showed good electrochemical activity and sensitivity. The high activity presented by the prepared material is probably related to the large specific surface area of the obtained sensor. The main advantage of using zeolites in the construction of biosensors is their ease of enzyme immobilization [29]. Moreover, the properties of zeolites can be easily modified by ion exchange and other methods, which are described in the next chapter of this work [30]. Thanks to their use, there is also no need to use toxic reagents, and it has been proven that, in some cases, they increase the sensitivity of the device [26].

Another biomedical use of zeolite materials is the creation of bone scaffolds for tissue engineering. Many studies show the use of zeolites for this purpose. They are often added to a biopolymer matrix of e.g., chitosan or gelatin [31]. For instance, Akmammedov et al. prepared a scaffold consisting of a chitosan matrix and zeolite A as a filler [32]. The results obtained show that the material is biocompatible; however, further in vivo studies are needed to show the full application potential. An interesting application of zeolites as scaffolds for tissue culture was presented by Wang et al. [33]. For the preparation of the material, he used a VPI-7 zeolite exchanged with silver ions, in which all aluminum atoms in the zeolite framework were replaced with zinc atoms. The scaffolds obtained by him showed good antibacterial activity.

Qing, et al. [34] prepared a stainless steel scaffold using 3D printing. Then the surface of the obtained material was covered with zeolite A, which was subjected to ion exchange with Ag^+ ions. The results obtained by the authors showed that the scaffolds have excellent antibacterial properties and good biocompatibility.

3. Modification of Zeolite Properties

Zeolites are materials that can be easily modified to obtain satisfactory properties. Many modification methods make it possible to obtain zeolites suitable for specific applications. Principal examples are modifications to obtain antibacterial properties, to immobilize enzymes and to obtain fillers for polymeric materials [28,35,36]. The easiest way to modify them is ion exchange, because, as mentioned before, the cations are not permanently bound in their crystal lattice and can be exchanged with any positively charged ion. An example of such a modification has been shown in many research papers. For example, Zhu et al. modified zeolite 13X with various metal ions, e.g., Cu^{2+}, and Ag^+ what facilitate the adsorption of organosulfur compounds [37]. The results showed that the silver-containing zeolites had a greater capacity than the zeolites containing another metal ion and had a capacity more than twice the capacity of the unmodified zeolite. Due to the use of ion exchange, zeolites can also gain antibacterial properties. Demirci et al. prepared A and X zeolites with different silicon to aluminum ratios, which were then ion exchanged with Zn^{2+}, Cu^{2+}, and Ag^+ ions. The anti-bacterial tests showed that all zeolites received anti-bacterial properties [35]. There are also further examples of increasing the functionality of zeolites through ion exchange. In another work, authors used zeolite X and A with substituted calcium ions as a carrier for an anti-osteoporosis drug. In this work, they proved that unsubstituted zeolites containing sodium ions are not able to retain the drug on its surface [5].

Another method of zeolite surface functionalization is silanization. It is a very easy method of surface functionalization used for many materials. This method uses so-called silanizing agents which have the desired functional groups; these agents react with the surface of the material, making it functional [38]. Many research studies show the application of this method to the functionalization of zeolites. Mahmoodi and Saffar-Dastgerdi presented the functionalization of sodalite zeolite with (3-aminopropyl) triethoxy silane [39]. Studies have shown that functionalized materials can absorb much larger amounts of toxic dyes than materials with an unmodified surface. In another work published by Buchwald et al. authors modified 13X zeolite with [3-(methacryloyloxy) propyl] trimethoxysilane [36]. Modified materials were used to prepare dental composites. The test results showed that the composites containing the modified zeolites have better mechanical properties than their unmodified counterparts.

The last method of zeolite surface modification presented in this work is the use of diazonium salts. This method has also found application in the modification of various surfaces, e.g., carbon, metals, and oxides. This technique enables surface functionalization with the help of various functional groups, e.g., amine, sulfone, hydroxyl, and carboxyl [40]. There are various examples of the use of this method for the modification of zeolites. Materials functionalized by this method are mainly used as fillers in polymeric materials. For instance, one study modifies 13X zeolite for use in the synthesis of dental composites. The purpose of the modification was the introduction of active dimethyl amino groups that would allow the creation of a covalent bond between the filler and the components of the polymer matrix [41]. Another example of zeolite modification by this method is a modification with diazonium salt obtained in situ from 2- or 4-amino benzyl alcohol. The obtained materials were used as fillers in phenolic resins. The test results showed that zeolites modified with 4-aminobeznyl alcohol, subjected to drying at elevated temperature, show much better mechanical properties than unmodified materials [42].

4. Zeolites in Modification of Titanium Alloy

A large part of the population, especially the elderly, suffer from bone diseases such as osteoporosis, rheumatoid arthritis, or bone cancer. There are also serious accidents associated with the formation of serious fractures. Often, in such cases, it is necessary to use an implant to replace a broken or diseased bone [43]. For this purpose, many materials have been created that can be used to create implants, for example, ceramics, polymers, and metals. However, often the first choice is implants made of titanium, and more specifically of the Ti6Al4V alloy. This alloy is characterized by excellent mechanical properties, very high resistance to corrosion in biological fluids, and biocompatibility [44]. Research by scientists around the world indicates a high survival rate of these implants but also indicates some imperfections. Titanium is bio-inert, which means that it does not cause allergic reactions; however, it is still recognized by the body as a foreign body. This causes the body to isolate the implant in the fibrotic capsule, which slows down osseointegration, prevents bone regeneration, and causes inflammation of the tissues around the implant [43,45]. In addition, the use of implants is associated with the risk of bacterial or fungal infection, as a biofilm may occur on the surface of the material used as an implant [46,47].

The above-mentioned disadvantages led scientists to try to functionalize the implant surface to improve bio-compatibility, osseointegration, and stop the formation of biofilm. The properties of the obtained layers are influenced by many parameters, such as surface topography, hydrophilic-hydrophobic properties, and surface energy. These properties are of great importance as they influence cell survival, which is crucial for rapid osseointegration [48]. Examples of titanium modifications include electrochemical synthesis of titanium oxide doped with Ca^{2+} and Sr^{2+} ions, preparation of sodium, calcium, and zinc titanate layers, and synthesis of organic metal networks on a metal surface, e.g., ZIF-8 [49–53]. One of the modifications that have also been proposed by the researchers is the synthesis of a zeolite layer on the implant surface. Applications of this type of layer are shown in the Figure 3.

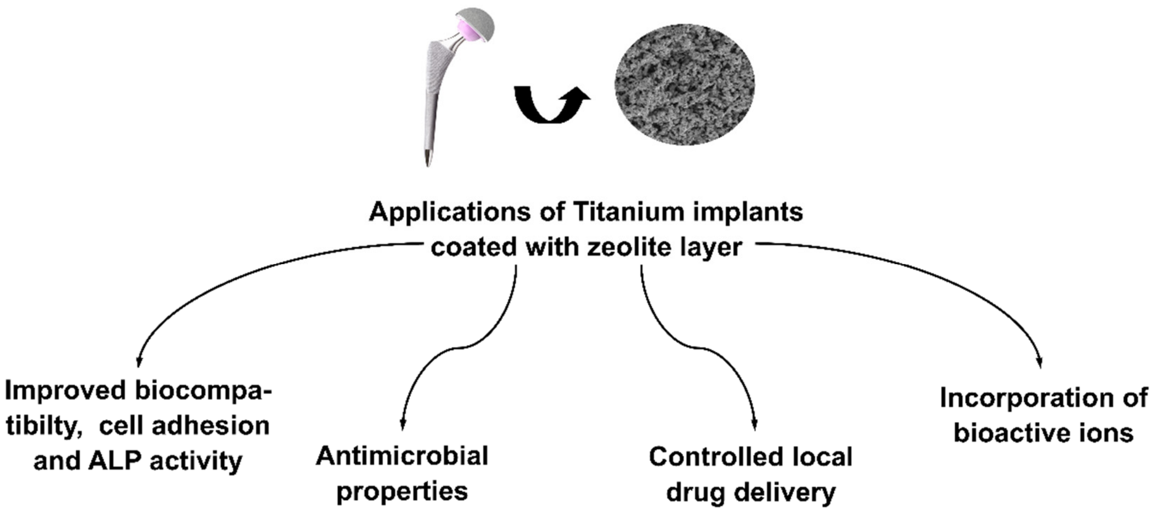

Figure 3. Applications of titanium implants coated with zeolite layer.

The first example of the use of zeolites as coatings for implants is the work prepared by Li et al. [54]. They modified the surface of the Ti6Al4V alloy with the use of zeolite with an MFI network structure. This coating was synthesized by the hydrothermal method. They also made extensive physicochemical and biological characteristics. Research has shown that materials modified with a zeolite layer have a greater ability to build up hydroxyapatite than uncoated materials. After 4 days of incubation in simulated body fluid (SBF), no hydroxyapatite (HAp) crystals could be seen on the titanium plate without modification, while large HAp crystals could be seen on the modified plate. The paper shows the effect of the obtained layer on the proliferation and migration of cells. It was found that modified titanium plates show higher biocompatibility and promote cell migration. The activity of alkaline phosphatase (ALP) and the expression of bone-related genes were also tested. The results show a significant increase in ALP activity and a significant increase in the expression of bone-related genes in the studies performed with the modified samples.

The next presented work also shows the use of zeolite with an MFI network in the modification of the same titanium alloy [55]. In this work, in-situ crystallization at room temperature was used to synthesize the layer. The successful synthesis of the zeolite layer was confirmed by X-ray radiation diffraction (XRD). The results of the study of the adhesion of the zeolite layer to the titanium show a very strong bond at the interface between the zeolite layer and the alloy. Authors presented also extensive biological and physicochemical characteristics. However, it was shown how the zeolite layer influences the corrosion resistance properties of titanium alloy. Corrosion tests showed much lower corrosion current density for the sample covered with the MFI zeolite layer compared to the uncovered sample. Additionally, after a 7-day incubation of samples in SBF in materials not covered with a zeolite layer, the value of corrosion current density increased significantly while in the coated materials it remains unchanged. In addition, the samples coated with MFI zeolite had a lower corrosion potential than bare Ti6Al4V. Biocompatibility studies also showed enhanced cell development when incubated with zeolite-coated samples. Observation of cell morphology also suggests increased adhesion to the zeolite layer.

The second type of zeolite that was used to modify the surface of titanium implants is type A zeolite. This zeolite has good ion-exchange properties due to the low silicon to aluminum-ratio [17]. In the work presented by J. Wang et al. on the surface of the titanium alloy, the hydrothermal synthesis of zeolite A was carried out, which was then ion exchanged with silver cations. The resulting coating was intended to have antibacterial properties that are desirable in the construction of such materials. Coating synthesis and success in ion exchange have been confirmed by various research techniques. Conducted research confirmed that the obtained layer is very stable in SBF, and morphological changes weren't observed. The study tested the release of antimicrobial silver ions; it was found that 72.8% of incorporated Ag^+ was released after 6 days. Antibacterial tests have shown that only the material containing silver ions has antibacterial properties, while the material coated with zeolite before ion exchange and unmodified material does not have a significant antibacterial effect. The influence of the obtained coatings on the adhesion of bacteria to the implant surfaces was also checked. Silver ion-containing material was also the best material to prevent adhesion, but titanium coated with zeolite before ion exchange also significantly reduced the adhesion of bacterial cells to the implant surface. As such a behavior may be due to the hydrophilicity of the obtained layers, the authors measured the contact angle. It turned out that the material modified with the zeolite itself and the material after ion exchange have very low contact angles (less than 10%), which means that the surface is very hydrophilic. It explains the significant influence of the obtained layers on the adhesion of bacteria to the surface. Silver may have cytotoxic properties, however, results of the biocompatibility studies indicated that the prepared material has low cytotoxicity and can be considered a safe material [56].

Local drug delivery has many advantages over systemic delivery. There are many controlled drug delivery systems, from titanium implants for various pharmaceutically active substances. Research shows that this approach can increase osseointegration [57,58]. The use of a titanium implant covered with a sodalite layer as a controlled drug delivery system for the drug against osteoporosis—risedronate (RSD) was also presented. The authors prepared titanium plates covered with a layer of sodalite zeolite. XRD studies showed high crystallinity of the obtained layers. Scanning electron microscopy images shows uniform distribution of zeolites on titanium alloy and the presence of macropores. The presence of macropores in the prepared layer is very important because such a structure accelerates bone growth. The prepared materials were ion-exchanged with Ca^{2+} ions. The next step was the drug loading step, it was proved that the drug is only retained on ion-exchanged materials. The drug release studies showed that it was released in a very slow manner. About 30% of the retained drug was released during the 219 days of the study, the authors predict a total release time of 2 years [59].

The next work that presents the hydrothermal synthesis of zeolite on the surface of titanium is that prepared by Li et al. [60]. In their work, they prepared the silicalite—1 zeolite coating. They also modified the obtained coating in such a way that they added Ca^{2+} ions during the crystallization of zeolites. The coating was confirmed using XRD, the test also allowed to state that the addition of calcium did not significantly affect the crystal lattice of the resulting zeolite. Investigations of the corrosive properties in an aqueous NaCl solution showed that the material with the zeolite coating releases almost two times less amount of toxic aluminum and vanadium ions than the material without the coating. Biological studies carried out on rabbit bone marrow mesenchymal stem cells (r-BMSCs) showed that a coating made of this type of zeolite also has very good adhesion properties to the cells. It was also found that the coated samples significantly accelerated the proliferation of cells as compared to the uncoated samples.

The last work presented in this review is that prepared by Wang et al. [61]. In their work, they modified porous titanium implants obtained by 3d printing with zeolite A. In this work, the obtained zeolite layer was also modified by ion exchange, this time strontium ions were used. The obtained materials were characterized in terms of physicochemical and biological properties. Both in-vitro and in-vivo tests were performed. Obtaining the desired type of zeolite was confirmed by the XRD technique. The contact angle tests were also carried out, the results showed that the titanium coated with zeolite has very high hydrophilicity, while the materials with exchanged ions have lower hydrophilicity. The release of Sr^{2+} ions was also checked. The greatest number of ions was released on the first day, then the release slowed significantly. The growth of hydroxyapatite was also investigated. It was found that only materials modified with zeolite layer are covered with HAp crystals after 14 days of incubation in SBF. In-vitro biocompatibility studies confirmed the results obtained by other research groups. The zeolite-coated materials show excellent adhesion to osteoblasts of rabbit bone marrow mesenchymal stem cells. To study the effect of the modification on a living organism, the obtained implants were implanted into rabbit condyles. The results of these studies showed that an implant modified with a zeolite layer shows better activity than a bare implant, and moreover implants modified with Sr^{2+} ions provide the fastest osseointegration.

All methods of titanium alloy modification and their influence on the final properties are summarized in Table 1.

Table 1. The influence of zeolite layers on the properties of titanium alloys described so far in the literature.

Titanium Alloy Type	Zeolite Type	Ion in Zeolite Structure	Influence of Modification on Material Properties	Ref.
Ti6Al4V	MFI	-	improvement of the growth of hydroxyapatite, higher biocompatibility, promote cell migration, increase in the expression of bone-related genes	[54]
Ti6Al4V	MFI	-	lower corrosion potential, enhanced cell development, higher biocompatibility, improvement of cell adhesion	[55]
Ti6Al4V	A	Ag^{+}	antibacterial properties, low cytotoxicity, biocompatibility	[56]
Ti6Al4V	Sodalite	Ca^{2+}	controlled long drug release (risedronate release),	[59]
Ti6Al4V	Silicalite-1	Ca^{2+}	releasing less toxic ions, very good adhesion properties to the cells, significant acceleration of cell proliferation	[60]
Ti6Al4V	A	Sr^{2+}	improvement of the growth of hydroxyapatite, excellent	[61]

5. Conclusions

This review indicates the high impact of modification of titanium implants on their properties. Materials modified with zeolite layers are characterized by a much better adhesion of cells to the surface of implants, increased alkaline phosphatase activity, and expression of bone-related genes. In-vitro studies show accelerated growth of hydroxyapatite on the surface of zeolite-modified implants, which is also confirmed by in-vivo studies, which also showed accelerated osseointegration of zeolite-modified materials. The corrosion properties have also been checked, which shows that zeolites have protective properties and slow down corrosion and prevent the release of toxic vanadium and aluminum ions. This review also showed how easily the properties of the obtained layers can be changed utilizing ion exchange to obtain the desired properties, e.g., antibacterial or the use of ion-exchanged zeolites as drug carriers.

It was also shown how many possibilities still exist, for example, the only ions that have been used to modify the zeolite layers are Ca^{2+}, Sr^{2+}, and Ag^{+}, while there are many more bioactive ions such as La^{3+}, Zn^{2+}, and Cu^{2+}. The layers on the surface of the titanium alloy should be prepared in the future also with the use of other synthetic zeolites, not only those presented in this paper. There are over 200 synthetic zeolites described in the literature, and each type can allow for obtaining a material with unique properties. When designing such layers, it is only necessary to take into account that some of the zeolites are cytotoxic (e.g., erionite) and are not suitable for this application [13]. Zeolite layers have so far been used only as carriers for anti-osteoporosis drugs, but it is also possible to use them as layers for antibacterial substances. The presented review shows that zeolites can be modified in various ways (e.g., silanization, diazotization, ion exchange). It is also possible to synthesize zeolites containing mesopores, which can open up to new applications of zeolites in the modification of titanium implants, e.g., drug delivery systems for new compounds. This is why we hope that this review will help academic scientist in creating new layers of zeolites and their new modifications on titanium implants with even better properties.

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