



Physicochemical Properties of Copper Modified Zeolite

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1. Introduction

Zeolites have been used in environmental engineering mainly in catalytic processes and as ion exchangers in water and wastewater treatment. A number of papers on the application of natural zeolites in chemical processes, especially modified zeolites, as heterogeneous catalysts (or their supports) have been published during last decades (Amiri & Nezamzadeh-Ejhi 2015, Świdowska-Dąbrowska & Schmidt 2014, Świdowska-Dąbrowska 2015, Świdowska-Dąbrowska et al. 2017). Moreover, modified zeolites have been increasingly often used in processes of water and wastewater treatment, as selective adsorbents (Hawash et al. 2018, Inglezakis et al. 2004, Li et al. 2009, Liu et al. 2017, Schmidt & Anielak 2011) or antibacterial material (Yao et al. 2019). Selective modified zeolites allow significant improvement in the effectiveness of impurities' removal without introducing additional reagents to the environment. The final effect of treatment of water solutions is determined by the catalyst used, its physicochemical properties and the process parameters. The catalytic activity of zeolites and their chemical stability strictly depend on the method of their modification and calcination temperature.

Modification of zeolites' surface is most often carried out using ion exchange, wet impregnation or precipitation methods. Aqueous ion exchange allows introduction of metal ions in place of interstitial cations, however, it requires a long time of zeolite contact with the salt solution and generates significant amount of residual solvent. The problem of wastewater, often containing heavy metals, harmful to the natural environment, may be solved by application of wet-impregnation method. Moreover, this method allows to control the amount of metal ions introduced into the zeolite framework (Singh et al. 2018). The third method – precipitation – creates deposits of metal oxides on the surface of zeolites. They are formed using a precipitation agent, e.g. NaOH, Na₂CO₃ or NH₃.

Depending on the used zeolite modification method, metal ions, hydroxocomplexes or oxides may form on its surface. Singh et al. used Cu/Zeolite Y (obtained using various methods) for the oxidation of quinoline in the catalytic wet peroxide oxidation process. They proved that the ion exchange and wet-impregnation methods lead to the formation of isolated Cu(I)/Cu(II) species. Such zeolites show bigger catalytic activity than zeolite modified with precipitation-impregnation method, despite increase of its specific surface, due to the deposition of large CuO crystallites on its external area (Singh et al. 2018).

The catalytic activity of metal oxide-based heterogeneous catalyst largely depends on the degree of dispersion of metal oxides on the surface of the zeolite. Xin et al. modified the SBA-15 zeolite with Cu(II) ions using NH_3 as a precipitation agent. It was dosed in a Cu/ NH_3 ratio from 1/3 to 1/6. The highest CuO dispersion on external area was obtained at the highest Cu/ NH_3 ratio. Strong interactions between Cu and zeolite, in such case, increased the thermal stability of the catalyst up to 700°C (Xin et al. 2018).

The dispersion of metal on the surface of zeolite also depends on the type of metal salt applied. Xuanwen et al. achieved higher degree of Cu dispersion on the surface of 13X zeolite using CuCl_2 for impregnation than $\text{Cu}(\text{NO}_3)_2$. For copper (II) chloride, Cu(II) species were found on the zeolite surface, while in the other case it might be CuO or basic cupric nitrate, which during calcination showed a tendency for aggregation (Xuanwen et al. 2017).

Batistela et al. noticed that the location of metal oxides on the zeolite surface also depends on the size and volume of its pores (Batistela et al. 2017). They conducted humid impregnation with zinc nitrate of three types of zeolites: NaY, NaA and ultrastable Y zeolite (containing Na^+ and H^+ ions) – USY, which were then calcined at 550°C. Studies of the surface structure of modified zeolites showed the presence of ZnO in micropores, which caused a decrease in the specific surface of zeolites. However in the case of NaA zeolite (which has a small volume of micropores), after full cavity saturation of micropores, ZnO crystallization also took place on the external surface of NaA. Supporting of ZnO on NaY and NaA did not significantly affect their photocatalytic activity – the bandgap value of ZnO/zeolite is similar to ZnO only (3.2 eV). On the contrary, an increase in the band gap value in relation to ZnO, was noted for USY. This requires usage of a stronger source of radiation and may cause the photocatalysis process to be unprofitable (Batistela et al. 2017).

Research conducted by Batistela et al. proved that the efficiency of zeolite modification is significantly affected by the first stage – pretreatment, i.e. preparation of the initial form of zeolite. Liu et al. showed that washing of the natural zeolite with acid causes unblocking of its pores (due to removal of impurities) and increase of the specific surface area of zeolite as well as increasing the number of active sites for adsorption process. The exchange of interstitial cations

(mainly metals of I and II groups of the periodic table) for H^+ ions causes strong protonization of zeolite, which promotes adsorption of NO_2^- anions on the surface of the obtained zeolite (Liu et al. 2017).

Sometimes it is also advisable to carry out calcination process before modification of the zeolite surface with metal ions. Studies of Sushkevich & van Bokhoven proved that the removal of carbonaceous impurities during the calcination of modernite prevents the loss of active Cu(II) ions, which can be reduced to Cu(I) during reaction with carbonaceous compounds. Moreover, calcination in pure oxygen atmosphere is preferred over the air. Air contains traces of organic substances that can be adsorbed on the surface of modernite (Sushkevich & van Bokhoven 2018).

Calcination is usually the last stage of modification of zeolites surface. A slight change of calcination temperature brings about considerable changes in its structure. Chen et al. (Chen et al. 2008) proved that zeolite catalytic activity and their chemical stability strictly depend on the method of their modification and temperature of calcination. Considerable decrease of catalytic activity of a zeolite after calcination at the temperature of $550^\circ C$, resulting from total dealumination of the zeolite was observed.

Effectiveness of modified zeolites in water and wastewater treatment also depends on surface charge, which is affected by forms of particles and molecules occurrence on its surface in function of calcinations temperature. Surface charge of zeolite is also affected by potential-forming ions, present in the treated solution, such as H^+ and OH^- (Ates et al. 2018, Świdorska-Dąbrowska & Schmidt 2012a).

Removal of individual impurities depends on their size, which determines easiness of their migration via the channels of clinoptilolite (Inglezakis et al. 2004, Erdem et al. 2004). However, there are only a few publications on the physicochemical properties of modified zeolites and their effect on aqueous solutions. It is very important in terms of their practical and technological application because the mechanism of impurities' removal from aqueous solutions using zeolites, for example in hydrogenous form (Liu et al. 2017) is different than that on a zeolite modified with Fe ions (Akgul 2014, Hawash et al. 2018, Świdorska-Dąbrowska et al. 2012b), Mn ions (Anielak & Schmidt 2015, Skoczko et al. 2015) or Co ions (Świdorska-Dąbrowska & Schmidt 2013, Andriyevskyy et al. 2018).

Practical application of a zeolite modified with Cu(II) ions in water and wastewater treatment may significantly increase effectiveness of sorption and oxidation of organic pollutants. Therefore, the aim of this study was to compare the physicochemical properties of natural zeolites modified by Cu(II) ions using two precipitating reagents: sodium hydroxide and sodium carbonate. This study evaluates the effectiveness of zeolite modification methods as well as their physical and chemical stability, taking into account the changes that take place during the process of calcination within the temperature range from $250^\circ C$ to $650^\circ C$.

2. Research methodology

2.1. Materials

Natural zeolite – clinoptilolite from Slovakia, with granulation size from 0.40 mm to 0.75 mm, containing 64.9% of SiO_2 , 9.9% of Al_2O_3 , 2.9% of K_2O , 2.5% of Na_2O , 1.4% of CaO , 1.4% of Fe_2O_3 and 0.3% of MgO , was used in the experiments.

All chemical reagents of an analytical grade: copper (II) sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), sodium carbonate decahydrate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) and sodium hydroxide (NaOH) were purchased from POCh Gliwice. Model solutions were prepared using ultrapure water (Hydrolab, Polska).

2.2. Modification of zeolite

The natural zeolite was transformed into the hydrogenous form by shaking it for 2 hours in 5% HCl solution of volume three times of zeolite volume and was subsequently modified with copper (II) ions by precipitation using two precipitating agents: sodium hydroxide or sodium carbonate.

Method with NaOH – the zeolite was stirred with 0.05 mol/L of CuSO_4 for 4 hours at $\text{pH} = 3$ and at temperature of 50°C ; subsequently pH was increased up to 9.5 with 2 mol/L of NaOH and the solution was stirred for another hour. The zeolite was washed with deionised water three times and dried at a temperature of 105°C .

Method with Na_2CO_3 – solid Na_2CO_3 was added to 0.05 mol/L of CuSO_4 (1 mol:1 mol). After 1 hour of stirring at a temperature of 50°C , zeolite was added to the solution and stirred for another 4 hours. Subsequently, the zeolite was separated, washed with three portions of deionised water and dried at a temperature of 105°C .

Those procedures were repeated three times, and each time the content of copper in the zeolite increased. Then zeolite, modified by precipitation with NaOH (ZCu-1) or Na_2CO_3 (ZCu-2), was calcinated for 2 hours in a muffle furnace, at the temperature of calcination ranging from 250°C to 650°C .

2.3. Analytical methods

The electrokinetic potential (zeta potential ζ) of the zeolite particles (in suspension of finely ground zeolite $d < 0.04$ mm with concentration of 0.1 g/L) was measured by the method of phase analysis of dispersed laser beam using zeta potential analyser ZetaPALS (Brookhaven Instrument Corp., USA).

The microstructure of the zeolite surface and its qualitative composition were examined using JSM 5500 LV scanning electron microscope (JEOL, Japan), with EDS method.

Cu concentration was determined using Varian Spectr AA 20 plus atomic absorption spectrometer.

2.4. Leaching test

In processes of heterogeneous catalysis, which are carried out in the liquid phase, active species (e.g. metal ions) can pass from the catalyst surface to the liquid. Determination of the amount of leached metal ions can be helpful in assessing the chemical stability of the catalyst, its activity and its reusability (Sádaba et al. 2015). In addition, Yang et al. (Yang et al. 2017) proved that Cu(II) ions leached out during heterogeneous catalytic ozonation of organic pollutants may act as a homogeneous catalyst and affect the mechanism of the oxidation reaction. They also observed a significant effect of the solution matrix on the metal leaching process.

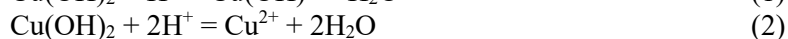
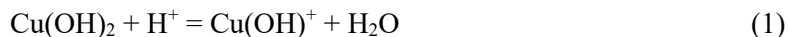
The leaching of metallic ion from the zeolite was determined in static tests, which involved stirring an aqueous suspension of zeolite (10 g/L) with the initial pH of 3, 6 and 9, for 24 hours. The pH of the solution was adjusted with 0.1 mol/L of NaOH or 0.1 mol/L of HCl. The resulting variables were pH and the concentration of copper in a decanted solution after a 24-hour shaking of zeolite with water solution.

3. Results and discussion

The method of zeolite modification significantly affects the copper content in a zeolite. Increase in the number of modification cycles is accompanied by an increase in the content of copper in ZCu-2 from approx. 3.5 to 9.5 mg/g of dry zeolite. On the contrary, Cu content in ZCu-1 is approx. 4 mg/g of zeolite and it does not change despite repeating the analytical modification procedure.

The process of precipitation at the final stage of modification of ZCu-1 zeolite was conducted at pH = 9.5 (pH was adjusted with NaOH solution). At this pH value, hydrated precipitable hydroxo complexes $\text{Cu}(\text{OH})_{2\text{aq}}$ dominate, increasing their concentration on the surface of zeolite (Fig. 1).

After 60 minutes of contact time of ZCu-1 zeolite with the precipitating solution, its pH decreased from 9.5 to approx. 5, when dissociated Cu^{2+} aqua ions dominate, whereas share of $\text{Cu}(\text{OH})^+$ is low (Fig. 1). Decrease of the solution's pH was a consequence of migration of protons from the zeolite matrix (zeolite in H form); they neutralised hydroxyl groups from dissociation of NaOH. Reactions (1) and (2) take place as a result of protons leaching:



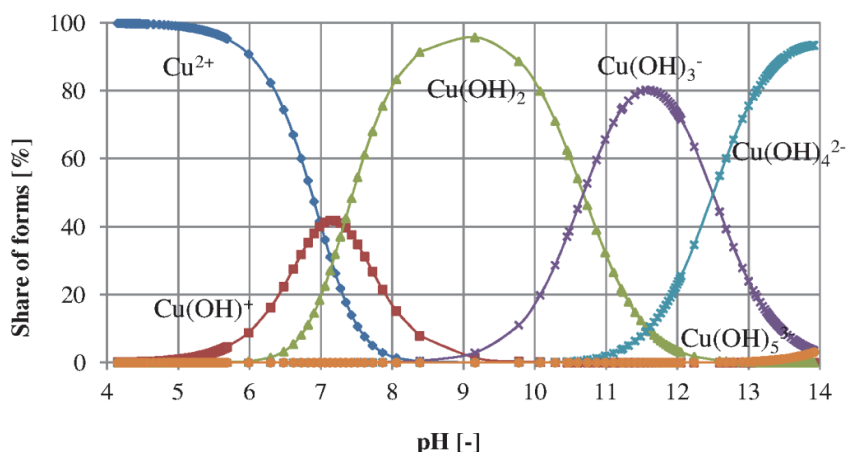


Fig. 1. Impact of solution pH on occurrence of Cu(II) complexes in aqueous solutions

As a result of proton migration processes the solution's pH decreases and precipitable complexes $\text{Cu}(\text{OH})_{2\text{aq}}$ (which occur on the surface of the zeolite) dissolve to $\text{Cu}(\text{OH})^+$ and Cu^{2+} (Cu^{2+} ions migrate into the solution). Such mechanism causes decrease of Cu concentration in zeolite, and copper present in the zeolite comes mostly from ion exchange processes.

ZCu-1 zeolite was modified in the following system: removal of ions from the zeolite with 5% solution of HCl (mainly Na^+ , K^+ , Ca^{2+} , Mg^{2+}), which comprise so-called zeolite contamination, modification with Cu(II) ions using method of coprecipitation and calcination. The process of calcination has a fundamental effect on the surface charge of a zeolite; it can either increase or decrease it. At the same time catalytic activity as well as the sorption capacity of ZCu-1 change. The results presented in Figure 2a indicate variable values of the zeta potential of examined ZCu-1 zeolite as the function of calcination temperature.

The ζ potential values of the ZCu-1 zeolite ranged from -25 to -45 mV in the pH range from 3 to 10.2. With the solution's pH increase from 3 to approx. 7.5, the potential decreased from -30 mV to -20 mV for ZCu-1 after calcination at temperature of 650°C, whereas its negative charge on the surface is higher and increases throughout the entire pH range after calcination at temperatures 450°C and 550°C. The difference probably results from dealumination process of the zeolite at the temperature 650°C, which change the Si/Al ratio in the zeolite and causes decrease of negative charge of zeolite surface. Changes in the structure of natural zeolite (modernite-clinoptilolite) during its calcination in the temperature range from 400 to 1000°C were studied by Wahono et al. (Wahono et al. 2019). They observed that at temperatures above 600°C the spe-

cific surface area of zeolite significantly decreased and the average pore size increased almost 4 times. However, at 1000°C the zeolite crystal transforms into cristobalite. Along with increasing calcination temperature, the Si/Al ratio did not change significantly. In turn, according to Tomazović et al., clinoptilolite in ammonium form undergoes the dealumination process at the temperature $\geq 400^\circ\text{C}$. In addition, they found that different cationic forms of Al are formed depending on the calcination temperature (Tomazović et al. 1996).

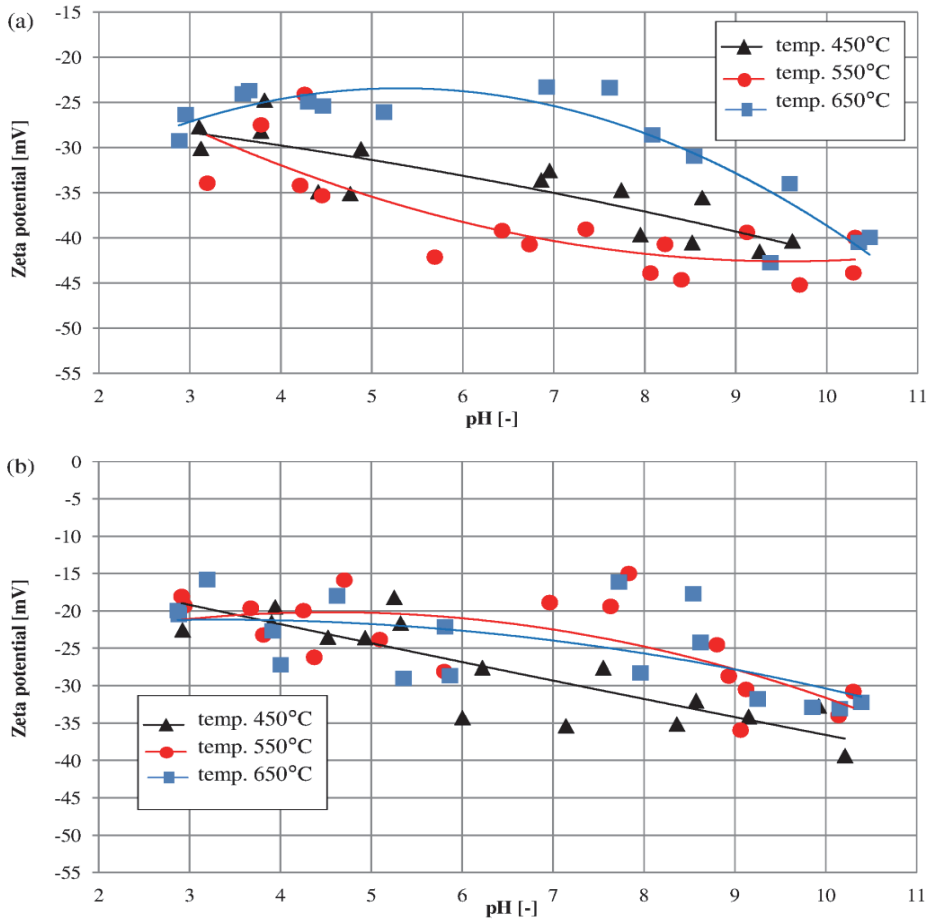


Fig. 2. Impact of solution pH on zeta potential of modified zeolite in function of calcination temperature: (a) ZCu-1, (b) ZCu-2

Moreover, our experiments have shown that the temperature of calcination from 250°C to 550°C does not significantly affect the zeta potential. Its value

depends on the concentration of potential-forming ions and presence of other ions in the solution. However, the surface charge of the zeolite is determined by H^+ and OH^- ions.

Changes of the solution's pH on the zeolite surface and in its pores can cause reactions (3-6):



Apart from migration of protons from the zeolite matrix, pH decrease is caused by reactions (3) and (5). According to reactions (3-6), Cu detainment in ZCu-1 is caused by electrostatic interactions between Cu(II) cations and the electronegative surface of the zeolite. Brönsted acid centres in the zeolite structure can lead to formation of $[Cu-O-Cu]^{2+}$ bridges. At $pH < 6$, when Cu(II) aqua ions dominate (Fig. 1), Cu is detained according to reactions (5) and (6).

Modification of zeolite with Cu(II) ions by coprecipitation with Na_2CO_3 results in the formation of insoluble, green-blue complex $Cu_2(OH)_2CO_3$ and $Cu_n(OH)_{2n-2}^{2+}$ in the aqueous solution. The pH value of the $CuSO_4$ solution from the initial value of 4.3 increased after adding Na_2CO_3 to $pH = 8$, and decreased to $pH = 7$ after 4 hours of contact time with zeolite. There were therefore favourable conditions for the precipitation of hydrated $CuCO_{3aq}$ ($pK_a = 6.5$), which could be adsorbed on the surface and in the pores of ZCu-2. The copper content in ZCu-2 zeolite increased steadily, reaching a value of about 9.5 mg/g of zeolite after the third cycle. The zeta potential analysis of ZCu-2 indicates that the zeolite had a lower negative surface charge throughout the entire range of pH changes as compared to ZCu-1 (Fig. 2). The zeta potential of the ZCu-2 zeolite ranged from -15 to -35 mV at pH range from 3 to 10.2.

In case of ZCu-2, the negative charge on its surface increases with the increase of solution pH and the decrease of calcination temperature (from $250^\circ C$ to $650^\circ C$). The ζ potential of ZCu-1 within the specific pH range has much greater absolute values, which vary from -30 mV to -45 mV. It can be concluded that electrostatic activity of ZCu-1 is higher than that of ZCu-2.

These relationships can be explained basing, among others, on formation of polymorphic species of copper (II) oxide. On the surface of ZCu-2 zeolite, which was obtained in precipitation with Na_2CO_3 method and calcined at temperature of $450^\circ C$, CuO dominates, hardly soluble in water. In an aqueous solution, the surface of the zeolite is hydrated, changing its surface charge. At $pH = 5$, when Cu^{2+} ions dominate (Fig. 1), the zeta potential was about -25 mV. As the pH increases further concentration of hydroxyl ions occurs in the diffusion layer of zeolite, and negative electrokinetic potential also increases.

At calcination temperature of 650°C, on the surface of ZCu-2 zeolite and in its micropores, dominate copper oxides γ -CuO and probably copper hydroxo oxide occurs (according to Wells) (Wells 1993). They form more stable connections with the zeolite matrix as compared to hydrated Cu compounds. A comparison of Figure 3a and 3b shows that Cu compounds, which form on ZCu-2 at lower calcination temperatures, migrate to the solution more readily at pH > 6. This may be caused by: (i) mechanical abrasion of copper oxide crystallites from the external surface of zeolite ZCu-2 during mixing, (ii) higher Cu concentration on the ZCu-2 zeolite surface (occurring in the form of CuO) than on ZCu-1.

Less Cu compounds migrate at lower initial pH (Fig. 3b), which is a consequence of the formation of acidic Brønsted active sites and detention of Cu in the zeolite matrix. Changes in the initial pH from 3 to 9 can result in reactions (3) and (4), which reduce the amount of copper leached to the solution.

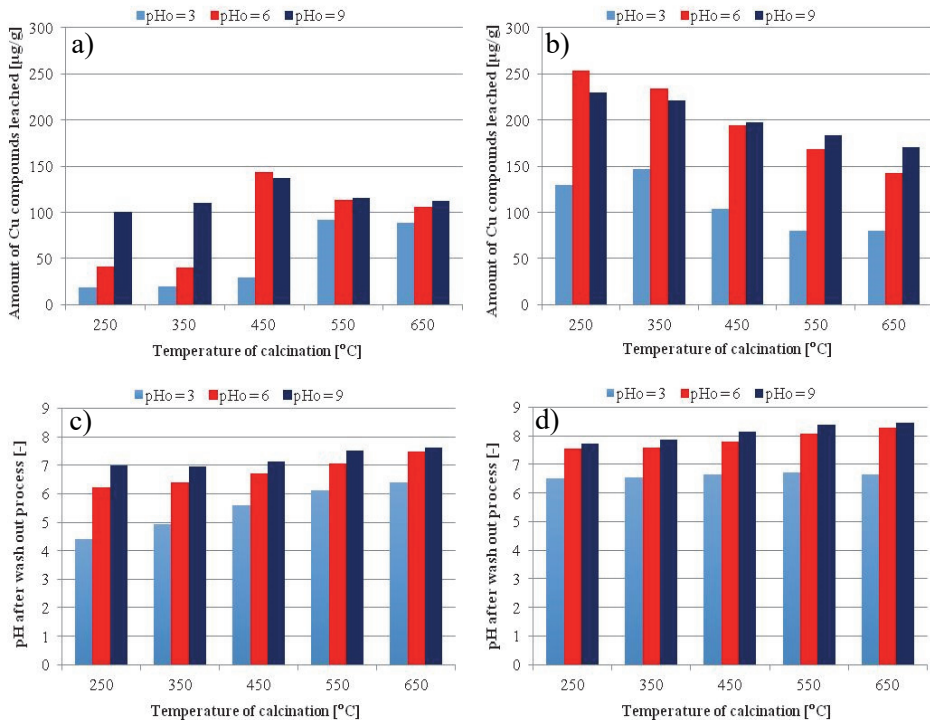
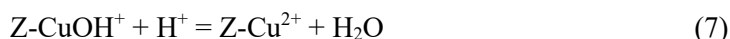


Fig. 3. Impact of calcination temperature of zeolite on amount of leached Cu compounds and pH after wash out process in function of initial pH of solution after 24 hour contact of zeolite with aqueous solution: (a, c) ZCu-1, (b, d) ZCu-2

Different relationships were observed for ZCu-1 zeolite (Fig. 3a and 3c). Migration of copper compounds from the zeolite matrix to the solution increases significantly only after calcination at temperature of 450°C. The copper content at lower calcination temperatures, at $\text{pH} \leq 6$, remains at a level of about 40 $\mu\text{g/g}$ of ZCu-1.

Compounds of copper (II) present on the zeolite surface (for the calcination temperature $< 450^\circ\text{C}$) undergo hydration to $\text{Cu}(\text{OH})_{2\text{aq}}$ in solution, which pH_{PZC} is from 9.5 to 10.2 (Kosmulski 2001). That is why, there is an excess of positively charged Cu-OH_2^+ groups in the solution and on the zeolite surface. Decreasing of the pH value below 5 brings about the process of jamming copper in the zeolite:



At higher calcination temperatures, stable forms of copper oxides $\gamma\text{-CuO}$ ($\text{pH}_{\text{PZC}} 7,5$) are formed on the zeolite surface (Kosmulski 2001), which can migrate to the solution as suspension, increasing the Cu concentration.

Study of the surface and pores of zeolites calcinated at temperature 650°C, performed with an electron scanning microscope, showed that ZCu-2 zeolite contains much more copper (approx. 5% wt.) as compared to ZCu-1 (0.12% wt.) – Figure 4.

Modification of zeolite using Na_2CO_3 as a precipitation agent resulted in sorption copper (II) carbonates on the surface of the zeolite, which during calcination decomposed into CuO , CO_2 and water. SEM images show numerous crystallites, mainly CuO , which is also confirmed by EDS analyses (high concentration of copper and oxygen) – Fig. 4b.

Analysis of the surface of ZCu-1 zeolite showed that it was covered with copper compounds in a small range (0.12% wt.). SEM image clearly shows crystals of clinoptilolite, the main component of natural zeolite, with a lamellar structure. However, several times larger amounts of copper were observed in its pores (0.72% wt.) – Fig. 4a, spectrum 2. Due to the low pH after the modification process, which favors creation of aqua and hydroxy ions of $\text{Cu}(\text{II})$, copper retention took place mainly due to ion exchange process. $\text{Cu}(\text{II})$ ions stuck in the zeolite channels were more strongly bound to the zeolite matrix than copper (II) ions retained at the external surface of zeolite. This a probable cause of their higher concentration in zeolite micropores.

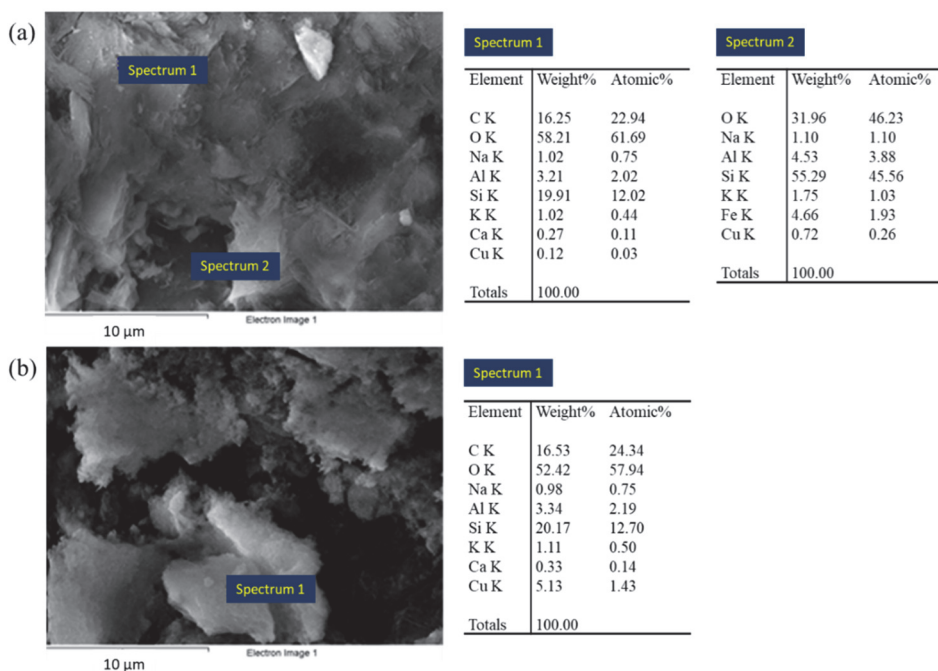


Fig. 4. Qualitative characteristics of examined zeolites after calcination at temperature 650°C: (a) analysis of ZCu-1 zeolite surface (spectrum 1) and inside of the pores (spectrum 2), (b) analysis of ZCu-2 zeolite surface

4. Conclusions

The results presented in this paper showed considerable differences in the physicochemical properties of clinoptilolite modified with Cu(II) ions by precipitation with NaOH (ZCu-1) and Na₂CO₃ (ZCu-2). Concentration of copper in the matrix of ZCu-2 zeolite is nearly three times higher compared to ZCu-1 as early as after the third modification cycle. Low concentration of Cu in ZCu-1 was caused by dissolution of precipitable complexes Cu(OH)_{2(aq)} to Cu(OH)⁺ and Cu²⁺ in the presence of proton derived from H-form zeolite. Cu was detained in ZCu-1 as a result of electrostatic interactions between Cu(II) cations and the electro-negative surface of zeolite. In ZCu-2 zeolite detention was caused by precipitation and coprecipitation of hydrated copper (II) carbonates (IV). Moreover, a significant effect of calcination process (at temperatures from 250°C to 650°C) has been confirmed, both on the surface charge of zeolite and on the amount and type of adsorbed copper. Various crystalline forms of Cu are formed. After calcination, on the surface of ZCu-2 in the function of temperature, polymorphic species

of copper (II) oxide occur, which form more stable connections with the zeolite matrix as compared to ZCu-1. After modification process, the electrostatic activity of zeolite ZCu-1 is higher than that of ZCu-2. Its value depends on the concentration of potential-forming ions (pH) and the presence of co-ions, which also affect leaching of Cu from the zeolite matrix to the solution. It was proved that migration of Cu was affected by reactions of hydration, hydrolysis and complexing of Cu with the zeolite matrix. Depending on the solution's pH, corresponding Cu complexes are formed which significantly reduces their content in the zeolite structure.

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Abstract

Zeolites have been used in environmental engineering mainly in catalytic processes and as ion exchangers in water and wastewater treatment. Selective modified zeolites allow significant improvement in the effectiveness of impurities' removal without introducing additional reagents to the environment. The final effect of treatment of water solutions is determined by the catalyst used, its physicochemical properties and the process parameters.

In this work effectiveness of zeolite modification methods as well as their physical and chemical stability, taking into account the changes that take place during the process of calcination within the temperature range of 250°C to 650°C is presented. A natural clinoptilolite used in the experiment was transformed into the hydrogenous form and subsequently modified with copper (II) ions by coprecipitation with NaOH and Na_2CO_3 . The effect of the method of the zeolite modification on Cu content, the zeolite Leaching capacity and surface charge was evaluated. An analysis of experimental results has shown that calcination temperature does not significantly change the surface charge, but does affect copper speciation. Analysis of EDS spectra by a scanning microscope, which showed that new and regular forms of copper compounds had been formed along the zeolite lattice structure is also presented.

The experimental results show that retention of Cu in zeolites was caused by electrostatic interactions between $\text{Cu}(\text{II})$ cations and the electronegative surface of the zeolite and coprecipitation of $\text{Cu}(\text{II})$ complexes.

Physicochemical properties of examined zeolites were affected by processes of hydration, hydrolysis and complexing of Cu with the zeolite matrix as a function of the solution's pH. Results show that the process of impurities' removal from water and wastewater depends on the method of zeolite modification and on the solution's pH.

Keywords:

zeolite, precipitation, surface modification, calcination, zeta potential, leaching

Właściwości fizykochemiczne zeolitu modyfikowanego miedzią

Streszczenie

W inżynierii środowiska zeolity stosowane są przede wszystkim jako wymiennicze jonowe w oczyszczaniu wody i ścieków oraz w procesach katalitycznych. Selektywne modyfikowane zeolity pozwalają na znaczące zwiększenie skuteczności usuwania zanieczyszczeń, jednocześnie nie wprowadzając dodatkowych reagentów do środowiska. O końcowym efekcie decyduje rodzaj zastosowanego katalizatora, jego właściwości fizykochemiczne oraz parametry prowadzenia procesu.

W pracy przedstawiono efektywność metod modyfikacji zeolitów oraz ich stabilność fizyczną i chemiczną, z uwzględnieniem zmian zachodzących podczas procesu kalcynacji w zakresie temperatur od 250°C do 650°C. W badaniach zastosowano zeolit naturalny klinoptylolit, który przeprowadzono w formę wodorową roztworem HCl, a następnie poddawano modyfikacji jonami miedzi (II) metodą współstrącania z użyciem NaOH i Na₂CO₃. Oceniono wpływ sposobu prowadzenia modyfikacji zeolitu na zawartość Cu, jego rozmywalność oraz ładunek powierzchniowy. Analiza wyników badań wykazała, że temperatura kalcynacji nie wpływa istotnie na zmianę ładunku powierzchniowego, ale na formę występowania związków miedzi. W pracy przedstawiono również analizę widm EDS wykonanych mikroskopem skaningowym, która pokazała, że wzdłuż struktury kryształicznej zeolitu zostały utworzone nowe i regularne formy związków miedzi.

Wyniki badań wykazały, że zatrzymywanie Cu w zeolitach zachodziło na skutek oddziaływań elektrostatycznych między kationami Cu(II) i elektroujemną powierzchnią zeolitu oraz w wyniku strącania i współstrącania kompleksów Cu(II).

Czynnikami wpływającymi na właściwości fizykochemiczne badanych zeolitów są procesy hydratacji, hydrolizy i kompleksowania Cu z matrycą zeolitu w funkcji pH roztworu. Przedstawiona w pracy analiza wyników badań wykazała, że proces usuwania zanieczyszczeń z wód i ścieków uzależniony jest od sposobu modyfikacji zeolitu oraz od pH roztworu.

Słowa kluczowe:

zeolit, strącanie, powierzchniowa modyfikacja, kalcynacja, potencjał dzeta, rozmywalność