

FTIR CHARACTERIZATION OF THE SURFACE ACIDITY OF ALFE - PILCS WHICH CAN BE USED AS CATALYSTS IN CHEMICAL AND ENVIRONMENTAL PROCESSES

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Abstract: The influence of iron ion content (Al/Fe ratio) and pH of the synthesis solution on the surface acidity of a series of AlFe-PILCs samples was investigated. The tests were performed by FTIR spectroscopic method, with identification of acidic centers by type. The samples were synthesized by the coprecipitation method and subsequently calcined. Mixed polyoxycations in the presence of basic synthesis solutions intercalate the host clay, resulting in mixed AlFe-pillars. It is assumed that as a result of coprecipitation at the selected Al/Fe ratios and synthesis conditions, a pillar space is formed with the simultaneous generation of strong acidic active centers of both Brönsted and Lewis types. It is assumed that coprecipitation with Al³⁺ in the presence of small amounts of iron ions causes modification of the acidity of the Al-PILC surface and development of acidity in relation to the host clay. The increase in the iron ions content during the synthesis of AlFe-PILCs causes a modification of the acidity in relation to Al-PILC and the host clay, as well as an approach of the total surface acidity of the formed AlFe-PILCs to Fe-PILC, with a very likely redistribution of acidity by type. Varying the pH of the synthesis solution significantly affects the development of surface acidity of AlFe-PILCs. It can be considered that the results of FTIR spectroscopy are correlated with the structure of the formed mixed pillars. The mixed pillar structure of varying acidity by type, depending on the examined synthesis parameters, provides the AlFe-PILCs samples with the potential of application in a wide range of acid-catalyzed reactions in the oil-petrochemical and basic chemical industry, but also in the field of environmental protection.

Key words: AlFe-PILCs; FTIR spectroscopy; surface acidity; acid centers; acid-catalyzed reactions; chemical and environmental processes

1. INTRODUCTION

The concept of sustainable industrial development requires control of the process of climate change, energy consumption, but also the development of modern methods applied to environmental protection. Over the last decades, a large number of studies have been published on pillared interlayered clays (PILCs) used as adsorbent materials and catalysts or supports for transition metals in heterogeneous catalysis [1]-[4]. Particularly, PILCs and AlFe-PILCs have been used for water treatment through advanced oxidation processes (AOPs) to remove organic pollutants [1]-[4]. They have also been studied in various chemical and environmental processes [1]-[4]. Wastewater from industrial plants has become polluted with very hazardous organic pollutants (for example phenols and its derivatives originating from the petrochemical industry, pesticides, toxic and bio-refractory azo-dyes [1]-[4], which, due to their great stability, are difficult to remove by conventional treatment methods. The future of wastewater treatment from stable organic pollutants belongs to methods based on the application of solid bi-functional AlFe-PILCs as eco-catalysts. AlFe-PILCs also are particularly promising candidates to replace conventional catalysts in certain acid-catalyzed reactions in the petrochemical and chemical industry hydrocarbon cracking, benzylation of benzene with benzoyl chloride, Friedel-Crafts reactions, and similar [1]-[4].

AlFe-PILCs are mixed pillar clays, obtained by intercalation, co-pillarization of montmorillonite natural clays with a mixed solution of two (aluminum and iron) polyoxycation species. The synthesis process of AlFe-PILCs pillar clay takes place by co-hydrolysis of aluminum and iron salts with simultaneous co-pillaring process. Large polyoxycations formed by partial hydrolysis perform ion exchange of small cations present in the interlayer space of montmorillonite [2],[5], while simultaneously increasing the interlayer basal distance in the resulting AlFe-PILCs. The intercalated polyoxycations are converted into metal oxide clusters, so-called pillars, during calcination. The

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resulting pillars are nanometer-sized columns that significantly affect the formation of the physicochemical, textural and catalytic properties of the resulting materials [2]-[5]. Pillars inserted between the montmorillonite layers expand the interlayer space, keeping it stable up to moderately high temperatures. As a result of the pillaring, a two-dimensional network porous structure is obtained, while simultaneously generating acidic active centers of both Brönsted and Lewis types [5],[6].

AlFe-PILCs belong to the so-called bi-functional catalysts because they consist of two phases with different functions during the reaction they catalyze. In this way, AlFe-PILCs shows the potential of application in both acid-catalyzed and redox reactions [5]-[6], applied in the chemical industry, energy technologies and in the field of wastewater treatment from industrial processes.

In this work, the influence of Al/Fe ratio and pH of the synthesis solution on the total surface acidity of a series of prepared and subsequently thermally treated (calcined at 300°C) samples of AlFe-PILCs was investigated. It was assumed that as a result of co-pillaring under selected synthesis conditions, mixed pillars of different Al/Fe ratios are formed, which provide pillar space, while simultaneously generating acidic active centers of Brönsted and Lewis type [6]-[8]. It was also assumed that co-pillaring with aluminum ions and with small amounts of iron ions causes the development of surface acidity in relation to the native clay but also to pure Al-PILC [9]. Increasing the iron ions content during the synthesis of AlFe-PILCs also causes the acidity of the surface of the resulting AlFe-PILCs to approach Fe-PILC, with a very likely redistribution of surface acidity types [6]-[9].

2. EXPERIMENTAL

2.1 Material and testing methods

Natural Ca-bentonite clay from Republika Srpska, was used as the starting material for the synthesis of the AlFe-PILCs series. The clay was previously prepared according to the methodology given in the literature [6]-[9]. The resulting clay enriched with the montmorillonite phase was the host clay for the preparation of AlFe PILCs.

The synthesis of a series of AlFe-PILCs with different content of iron ions (Al/Fe ratio) and at different pH values of the synthesis solution (OH/Al+Fe ratio) was performed by the co-pillaring process. The co-pillaring process is the simultaneous introduction of the polyoxycation pair, aluminum and iron ions, into the host clay [6]-[9]. The experimental synthesis conditions and labeling of the resulting AlFe-PILCs samples are shown in Table 1.

Table 1 – Experimental parameters of synthesis, composition and labeling of AlFe-PILCs

Sample label	pH of the synthesis solution (OH/Al+Fe, mol/mol)	Al/Fe ratio (mol/mol)
AlFe 9/1 (2)	2	9/1
AlFe 5/5 (2)	2	5/5
AlFe 5/5 (4)	4	5/5
AlFe 1/9 (2)	2	1/9

The total acidity of the surface of the series of AlFe-PILCs was examined by the FTIR spectroscopy after the adsorption of pyridine on acidic active centers, which are present on the surface of the samples in accordance with the method shown in the literature [6]-[9]. The FTIR spectroscopic tests of chemisorbed pyridine (in the area of 1400-1700 cm⁻¹) on AlFe-PILCs were used in order to test the total surface acidity of the synthesized samples, but also to differentiate the type of acidic active centers, Brönsted and Lewis type [6]-[9]. The following literature data on FTIR spectra [6]-[9] were used as starting points for FTIR identification of different types of acidic active centers on the surface of the synthesized series of AlFe-PILCs:

- Pyridine molecules chemisorbed on the Brönsted type are characterized by the presence of two bands at 1638 cm⁻¹ and 1545 cm⁻¹, which simultaneously represent the combination of the

valence vibration frequency of C-C bonds with C-H and N-H bonds in those groups, respectively.

- Characteristic bands appearing at 1452 cm^{-1} and 1580 cm^{-1} originate from pyridine chemisorbed on Lewis acidic active sites. They simultaneously represent a combination of C-C bond stretching frequencies with the in-plane C-H bond frequency.

The FTIR spectroscopic tests were performed on an IR spectroscope with Fourier transform type: Termonicolet Nexus 670 FTIR. The spectrum of each AlFe-PILCs was recorded, at the maximum sensitivity of the device, in the range of wave numbers of $1400\text{-}1580\text{ cm}^{-1}$ in accordance with literature recommendations for the range of wavelengths of interest for identification in this paper [6]-[9].

3. RESULTS AND DISCUSSION

The FTIR spectra of AlFe-PILCs (Table 1) in the region of wave numbers $1400\text{-}1580\text{ cm}^{-1}$, characteristic for the presence of acidic active centers on the surface, are shown in Figure 2-5. In order to more adequately compare and detect the generated mentions in the synthesized, mixed samples of AlFe-PILCs, the spectra of pure Al-PILC are shown in comparison (Figure 1); and Fe-PILC (Figure 6) which were taken from the literature [6]-[9].

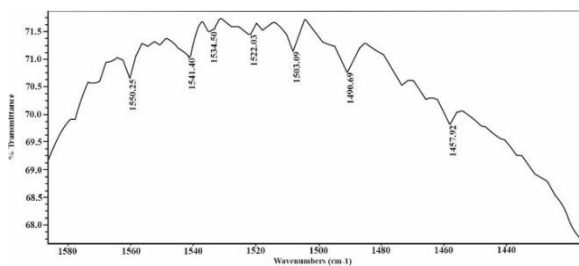


Figure 1 – The FTIR spectrum of Al-PILC

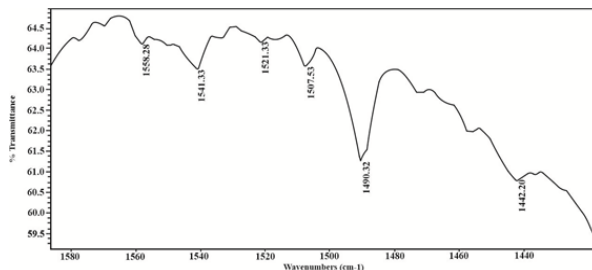


Figure 2 – The FTIR spectrum of AlFe-PILC 9/1 (2)

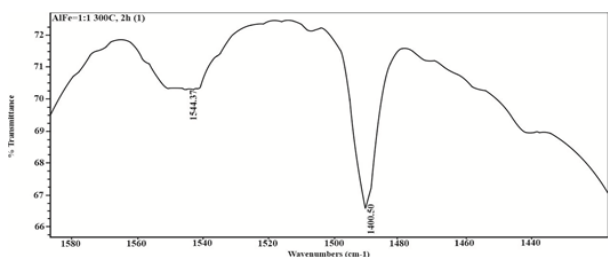


Figure 3 – The FTIR spectrum of AlFe-PILC 5/5 (2)

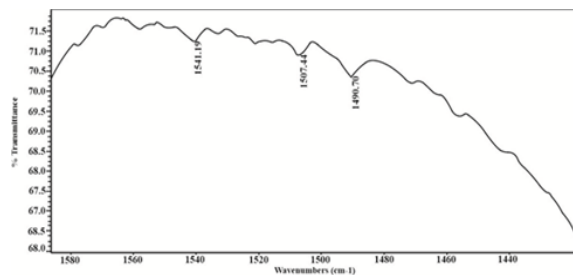


Figure 4 – The FTIR spectrum of AlFe-PILC 5/5 (4)

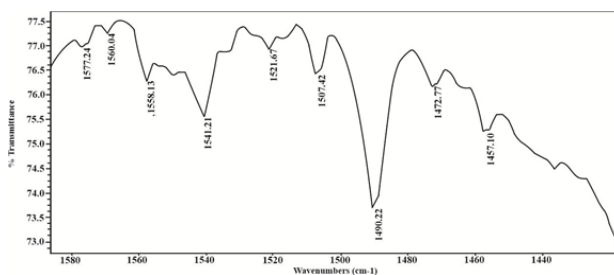


Figure 5 – The FTIR spectrum of AlFe-PILC 1/9 (2)

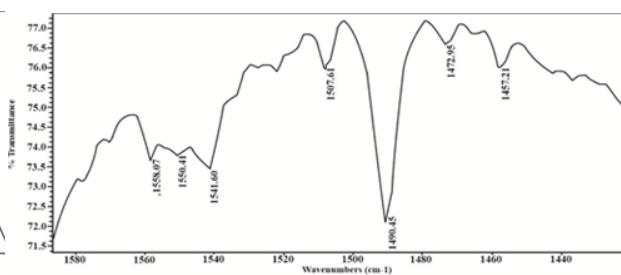


Figure 6 – The FTIR spectrum of sample Fe-PILC

In the area of the FTIR spectrum $1400\text{-}1580\text{ cm}^{-1}$, characteristic for the presence of acidic active centers on the surface of AlFe-PILC [7]-[9], differences in the appearance of the spectra of the examined series of AlFe-PILCs (Figure 2-5) compared to Al-PILC (Figure 1) were observed. The phenomenon could be explained by the influence of the presence of small amounts of iron ions in the samples (Figure 2-5) on the modification of the acidity of the Al-PILC surface (Figure 1). The phenomenon could also be considered a consequence of the creation of mixed AlFe-pillars in the structure of the synthesized samples. The degree of modification of the surface acidity of AlFe-PILCs samples (Figure 2-5) in relation to Al-PILCs and approaching the acidity present in Fe-PILCs (Figure

6) depends on the Al/Fe ratio present in the resulting mixed pillars and on the synthesis conditions (Table 1). An increase in the iron ion content in mixed pillars, i.e. a decrease in the Al/Fe ratio, causes the surface acidity of AlFe-PILCs samples (Figure 2-5) to approach the acidity present in Fe-PILC (Figure 6). The above can be clearly identified by the appearance and strength of characteristic bands for surface acid centers, present in the examined spectrum of the sample AlFe-PILC 5/5 (2) (Figure 3).

In order to examine the acidity on the surface of the synthesized AlFe-PILCs (Figures 2-5) but also to differentiate acidic centers by type, the observed spectrum area of $1400\text{-}1580\text{ cm}^{-1}$ was extracted at the maximum sensitivity of the device. The identification of the bands in that area of the spectrum was made based on the literature [8]-[9]. According to the above, in the region of wave numbers $1400\text{-}1700\text{ cm}^{-1}$ there is an adsorption band characteristic for the presence of Brönsted acidic active centers at 1540 cm^{-1} . The band characteristic for the presence of Lewis-type acidic centers is present at 1450 cm^{-1} . The adsorption band present at 1490 cm^{-1} indicates the joint, simultaneous presence of Brönsted and Lewis type acidity, and is always of well-defined intensity and sharpness.

The appearance of the obtained AlFe-PILCs spectra (Figures 2-5) is between Al-PILC (Figure 1) and Fe-PILC (Figure 6). The Al/Fe ratio determines whether the spectra of AlFe-PILCs are approaching or moving away from those of Al-PILC. In the spectra of Al-PILC (Figure 1) and the entire series of AlFe-PILCs (Figure 2-5) there are bands at characteristic wave numbers, which coincide with the starting ones for identification [8]. The bands belong to both the Brönsted and Lewis types of acidic active centers, which is consistent with the assumptions used in this paper.

However, as can be seen from the reference FTIR spectra (Figure 1, Figure 6) bands characteristic for the Lewis acidic type appear at approximately 1457 cm^{-1} in Al-PILC and in Fe-PILC, while in the series of AlFe-PILCs (Figure 2-5) depending on the Al/Fe ratio is used and the synthesis conditions ((OH/Al+Fe) ratio defined in Table 1) there is a shift in the position of that band to 1450 cm^{-1} . There is also the appearance of weaker signals for Lewis type acidic active centers in the spectral region $1442\text{-}1457\text{ cm}^{-1}$. Therefore, the increase in the content of iron ions (decrease in Al/Fe ratio) in the tested AlFe-PILCs (Figure 2-5) as well as the increase in the (OH/Al+Fe) ratio, causes a shift of the specified band from 1442 to 1457 cm^{-1} , which additionally becomes more stretched. The observed shift may indicate changes in the Lewis type of acidity with a change in the Al/Fe ratio. It was observed, namely, that in AlFe-PILCs with increasing the content of iron ions (decrease in Al/Fe ratio) a band for the Brönsted type of acidity appears in the spectrum at 1472 cm^{-1} , which is present only in Fe-PILCs (Figure 6) and that the spectra of modified pillars (Figure 2-5) in appearance approach the spectrum of Fe-PILC (Figure 6). It was noticed that the sample AlFe-PILC 9/1 (2) (Figure 2) is much closer to Al-PILC (Figure 1) in terms of the appearance of the spectrum, which could be explained by the fact that it contains mixed pillars with a higher Al/Fe ratio. This observation correlates with the previous observation, that is, the assumption used in this paper.

The results of the spectrum analysis (Figure 2-5) confirm that the change in the Al/Fe ratio in the series of tested AlFe-PILCs samples causes changes in the presence of Brönsted type acidity, and probably also in the presence of Lewis type acidity. The Brönsted type of acidic active centers occurs in all samples at 1540 cm^{-1} , while the introduction of iron ions does not cause a shift in the position of the mentioned band in the analyzed spectra.

An interesting analysis is the appearance of the band at 1490 cm^{-1} , characteristic for the common presence of both types of acidic active centers on the surface of Al-PILC (Figure 1) and AlFe-PILCs (Figures 2-5). A sharp band at 1490 cm^{-1} is present both in Al-PILC and in all AlFe-PILCs samples, but it is much more intense in AlFe-PILCs, which, according to the results of this work, may indicate certain changes in acidity that occurred by copulation, i.e., the formation of mixed Al-Fe pillars in the host clay. The intensity of the mentioned band also increases significantly with the increase in the content of iron ions (decrease in Al/Fe ratio) in the series of AlFe-PILCs, which is a very significant correlation with the assumption used in this paper.

Based on the results obtained in this work, it can be considered that the increase in Fe^{2+} content modifies the overall surface acidity of the resulting AlFe-PILCs in relation to Al-PILC and brings it closer to the acidity in Fe-PILC. The above confirms the initial assumptions used in this paper [6]-[9].

In this paper, in addition to the influence of the Al/Fe ratio, the influence of increasing the (OH/Al+Fe) ratio on the total surface acidity of the AlFe-PILCs was observed. In the sample AlFe-PILC 5/5 (4) (Figure 4) the band at 1490 cm^{-1} is much weaker in intensity compared to the same one in the sample AlFe-PILC 5/5 (2) (Figure 3). The observed phenomenon may indicate a decrease in total acidity with an increase in the basicity of the co-pillaring solution (at the same Al/Fe ratio).

Based on the results obtained in this paper, it can be considered that the used assumptions [6]-[9] were confirmed, except for the sample AlFe-PILC 5/5 (4). The process of co-pillaring with mixed AlFe-pillars leads to a significant increase in the total acidity of the surface of the tested AlFe-PILCs compared to montmorillonite. Also, on the surface of AlFe-PILCs (except in the sample AlFe-PILC 5/5 (4)) there are both Brönsted type and Lewis type acidic active centers, to a much greater extent than in montmorillonite, as the host clay. The obtained results are in accordance with the assumptions that montmorillonite has only slight surface acidity [6]-[9].

Based on the analyzes performed in this paper, it can be considered that the examined Al/Fe ratio have an influence on the change of the total acidity of the surface in the series of AlFe-PILCs in relation to Al-PILC and host clay. The examined Al/Fe ratios in the series of PILCs also significantly influence the distribution of surface acidity by type and indirectly predetermine the area of application in catalysis.

It must be emphasized that FTIR spectroscopy was used in this work only as a qualitative method for determining the type of acidic active centers present on the surface of AlFe-PILCs. The relationship between Brönsted and Lewis acid centers in the examined AlFe-PILCs was not studied in this paper.

4. CONCLUSION

The FTIR spectroscopic tests performed in this work showed that the total acidity of the surface, in a series of AlFe-PILCs, significantly depends on the examined Al/Fe ratios and the used synthesis conditions. It can be considered that at all examined Al/Fe ratios and at the ratio of (OH/Al+Fe)=2, there was an increase in the total surface acidity of the AlFe-PILCs samples compared to the slight acidity of the montmorillonite surface. In the examined AlFe-PILCs samples, an increase in the content of iron ions, but at a ratio of (OH/Al+Fe)=2, causes the total surface acidity of the examined samples to approach Fe-PILC with a simultaneous modification of the surface acidity in relation to AlFe-PILCs. The phenomenon could be explained by the fact that the resulting Al-Fe mixed pillars, with a higher content of iron ions, cause the development of total acidity in the tested AlFe-PILCs and that, in a less acidic environment. It can be considered that an increase in the (OH/Al+Fe) ratio at the same Al/Fe ratio causes a decrease in total acidity with an increase in the basicity of the synthesis solution, which may represent one of the elimination criteria when choosing the composition of samples for testing in specific catalytic reactions. In general, it can be considered that strong Brönsted and Lewis acid active centers on the surface are dominant in the examined AlFe-PILCs, which must also be taken into account when choosing the area of their application in catalytic reactions.

Based on the results of FTIR spectroscopic tests in this paper, it can be generally considered that the used Al/Fe ratios favorably influenced the development of the total surface acidity of the prepared series of AlFe-PILCs. The aforementioned opens up possibilities for further work in the direction of testing their catalytic activity in various commercial, acid-catalyzed reactions in oil-petrochemical and/or basic chemical industries, CWPO reactions applied to wastewater treatment and the like.

The further work could include: determination of the mutual ratio of Brönsted and Lewis acid centers in the tested AlFe-PILCs using FTIR spectroscopy as a qualitative method, characterization of the samples by physico-chemical methods and the like, with the aim of gaining the most complete insight into the possibilities of their catalytic application.

5. REFERENCES

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