CATALYTIC PROPERTIES OF A HEATED AMMONIUM-SATURATED DIOCTAHEDRAL SMECTITE

Ľuboš JANKOVIČ[1] and Peter KOMADEL[2,*]

Institute of Inorganic Chemistry, Slovak Academy of Sciences, 842 36 Bratislava, Slovak Republic; e-mail: [1] uachljan@savba.sk, [2] uachkomp@savba.sk

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Dedicated to Professor Ľudovít Treindl on the occasion of his 70th birthday in the recognition of his outstanding contributions to physical chemistry.

A series of acid catalysts was prepared by heating of NH_4-saturated montmorillonite at 200–600 °C for 24 h. Their catalytic activity was tested in acetylation of 3,4,5-trimethoxybenzaldehyde with acetic anhydride. This reaction is sufficiently sensitive to modification of the catalyst and thus suitable for testing catalytic activity of modified montmorillonites. Most of the prepared catalysts were able to catalyse the test reaction and produce diacetate in higher than 50% yields. The most active catalyst was obtained after heating at 300 °C. It was slightly less effective than commercially available acid-activated K10 catalyst.

Key words: Protection; Aldehydes; Acetylation; Thermal modification; NH_4-montmorillonite; Smectites; Aluminosilicates; Heterogeneous catalysis.

Most catalysts used by organic chemists are based on the naturally occurring smectites, the main minerals of bentonite ores. Smectites are swelling clay minerals; the best known of them is montmorillonite. This mineral has an aluminosilicate structure, which can be compared with a multilayer ham sandwich. The “bread” layers are the aluminosilicate layers where two external tetrahedral (mainly silica) sheets surround the internal octahedral (mainly alumina) sheet in a tetrahedral-octahedral-tetrahedral (TOT) structure. The “ham” is interlayers with cations and water. Montmorillonites are minerals in which isomorphous substitution of some of the octahedral aluminium(III) atoms with iron(III) and/or magnesium(II) atoms has taken place. Partial substitution of tetrahedral Si(IV) with Al(III) is also common. The Mg(II) and Al(III) in the octahedral and tetrahedral sheets, respectively, cause the negative charge of the layers. In the naturally occurring montmorillonites, this charge is balanced by hydrated interlamellar cations, such as Na^+ or Ca^{2+}. These cations are exchangeable and can be substituted with protons or various inorganic or organic cations. Some cations also occupy broken edge sites. An important property of smectites is swelling in the presence of either water or a host of organic molecules, when the interlamellar distance between the layers increases to accommodate the guest molecules[1,2].

The first industrial application of clays as catalysts date back to the beginning of the 20th century, while acid-treated smectites have been known for more than 50 years as catalysts for oil cracking[3]. Since the 1960's they have been partly replaced with zeolites, mainly due to a better zeolite activity and selectivity[4,5]. However, solid acid catalysts, in particular acid-treated montmorillonites, can be used to catalyse a wide range of important industrial processes, such as isomerisation, liquid refining and Friedel–Crafts alkylation, playing an increasing role in the move towards establishing environmentally friendly technologies[6].

Clay catalysts have been shown to contain both Brønsted and Lewis acid sites, with the Brønsted sites mainly associated with the interlamellar region and the Lewis sites mainly associated with edge sites. The acidity of smectites is influenced by the quantity of water between the layers[1]. If the catalyst is heated to about 100 °C to remove most of the interlamellar water, the Brønsted acidity increases markedly to that of strong acids. Heating to higher temperatures (200–300 °C) causes collapse of the interlayer structure as the water is driven out, generating a decrease in Brønsted but an increase in Lewis acidity. Further heating (>450 °C) results eventually in complete dehydroxylation of the aluminosilicate lattice[7].

A different kind of acidity is due to protons as exchangeable cations. In contrast to other cations, it is not easy to prepare the H-form of a smectite *via* ion exchange with an acid or a resin in the H-form[8]. H-smectites are unstable materials, protons attack the clay mineral structure and a part of the structural cations gets transferred into the ion-exchange sites. This effect occurs even under relatively mild conditions. For example, van Olphen found that the conversion of Wyoming montmorillonite with 0.01 M HCl at room temperature led to the 60% occupancy of the exchange sites by Al (ref.[9]). A way to overcome this acid leaching problem is to prepare the NH_4-form *via* ion exchange, followed by heat treatment at 550 °C (ref.[10]). The NH_4^+ ion decomposes, NH_3 evaporates and H-saturated smectite is prepared.

The effect of heating of H^+-exchanged clay minerals depends on the type of the layer silicate and on the preparation method of the H-form. In the case of montmorillonites, protons can migrate into vacancies in the octahedral sheet, where they associate with lattice oxygens[10,11]. In general, these protons are not accessible to catalysis, because the free diameter of the hexagonal hole in the tetrahedral sheet is only 0.26 nm (ref.[12]), thus protonation of reagents being very limited. After calcination, the acid sites left will be situated at edges, but their number will be substantially decreased. Higher stability was observed for materials prepared *via* calcination of NH_4-forms than for acid-treated or H-resin-exchanged catalysts[8,10].

A solid surface may interact with organic molecules also as a function of its hydrophobicity. A weak interaction precludes any catalytic step, while too strong bonding of organic products to the mineral surface makes desorption too slow or even impossible. The hydrophilic/hydrophobic character of the surface may be manipulated by an appropriate choice of the exchangeable cations[13].

The acid-treatment conditions corresponding to maximum catalytic activity depend on the precise reaction being catalysed[14,15]. Reactions between polar molecules require clays acid-treated under mild conditions or for short times, capitalising on the large number of acid sites available on the internal surface. In contrast, the surface accessible to non-polar molecules consists only of the external face and edge areas of the clay platelets. These reactions require more severely acid-treated clays and the catalytic activity depends on fine tuning of the changes in the surface area and decrease in the cation exchange capacity. However, in a swelling medium, optimum catalytic activity may be achieved not only through acid treatment, but simply by ion exchange with acid cations such as Al^{3+} ions; on the contrary, this last treatment has a negligible effect in a non-swelling medium[16].

The first step in the activation procedure, which is required for both natural and synthetic clay minerals, is to convert the clay into the desired ion form. In the case of metal ions, this can be done with relative ease by ion exchange using a concentrated solution of a suitable salt. The excess salt is removed by repeated washings. As an alternative, one can use ion-exchange resins in suitable ion forms.

There is still a great demand for acid catalysts under mild conditions and in environmentally friendly processes. Montmorillonites, a class of inexpensive and non-corrosive solid acids, have been used as efficient catalysts for a variety of organic reactions[17]. The reactions catalysed by montmorillonites are usually carried out under mild conditions with high yields and high selectivities and the workup of these reactions is very simple; only filtration to remove the catalyst and evaporation of the solvent are required. Montmorillonite catalysts are easily recovered and reused[18].

Some of frequently used organic reactants containing reactive groups, such as aldehydes, ketones, *etc.*, require protection of these groups to avoid undesirable side reactions. Protection of aldehyde with acetic anhydride[19] in the presence of an acid catalyst is a suitable reaction for testing catalytic activity of modified smectites. The aim of this work was to prepare catalysts of different acidity from a NH_4-saturated montmorillonite by heating at various temperatures and to test catalytic activity of these materials for the conversion of 3,4,5-trimethoxybenzaldehyde in acetic anhydride into diacetate.

EXPERIMENTAL

Montmorillonite separated from bentonite from deposit Ivančice (Czech Republic) was used for the experiments. Bentonite was ground in an agate mortar and <2 µm fraction was separated by sedimentation in order to remove most of the impurities. In the course of this process, the sample was repeatedly saturated with a calcium chloride solution to obtain a homoionic form of montmorillonite. The ammonium form was prepared from the Ca-form *via* multiple overnight saturation with 1 M NH_4Cl solution. Excess salt was removed afterwards by washing with distilled water until a negative test for chlorides with silver nitrate solution; the NH_4-saturated montmorillonite was dried at 60 °C and ground to pass a 0.2 mm sieve. The catalysts were prepared by heating the NH_4-form at 200–600 °C for 24 h (in steps of 100 °C).

Commercially available acid montmorillonite-based catalysts K10 and KSF were obtained from the manufacturer (Südchemie Moosburg, Germany). Solvents and chemicals were obtained from Merck (reagent grade) and were used as supplied.

All catalytic tests were performed in small glass flasks using 10 mg smectite immersed in 10 ml of a 0.1 M solution of 3,4,5-trimethoxybenzaldehyde in acetic anhydride. The reaction mixture was kept under stirring at 20 °C for up to 24 h. 10 µl portions of the liquid phase were removed from the flasks with a syringe, diluted to 1 ml with acetonitrile and analysed using HPLC chromatography. Blank experiments (without catalyst) were performed simultaneously. Three parallel catalytic experiments were carried out for each catalyst.

Analytical Methods

The prepared catalysts were ground to pass a 0.2 mm sieve and characterised by FTIR spectroscopy, X-ray diffraction and thermal analysis.

Fourier Transform Infrared (FTIR) Spectroscopy

The spectra were obtained on a FTIR spectrometer Nicolet Magna 750 equipped with a DTGS detector. For each sample, 128 scans were recorded in the 4 000–400 cm^{-1} spectral range in the transmittance mode with a resolution of 4 cm^{-1}. The KBr pressed disk technique (1 mg of sample and 200 mg of KBr) was used.

X-Ray Diffraction (XRD)

Powder specimens were analysed by XRD using a Philips PW 1710 diffractometer (Ni-filtered CuKα radiation).

Thermal Analysis

Simultaneous TG and DTA were conducted from ambient temperature up to 1 000 °C, using a T.A.I. SDT 2960 instrument (10–20 mg sample mass, 10 °C min^{-1} in flowing air).

HPLC Chromatography

Samples were analysed using a Hewlett Packard HP-1090M HPLC apparatus with a Hypersil column (BDS 5 μm/200 × 2.1 mm) and a mobile phase consisting of a mixture of water and acetonitrile. Detection was performed with a diode array detector at 210 nm and the products were identified by the retention times of reference substances. The separation of all analysed compounds is shown in a representative chromatogram (Fig. 1). Differences in the determined concentrations of the reaction products in three parallel runs were always within ±2% from the average used in the figures. The yield was determined as the percentage of the reactant converted to the reaction product.

RESULTS AND DISCUSION

The catalysts used in this study include heated NH_4^+-montmorillonites and commercial K10 and KSF, which are acid-treated montmorillonite-based catalysts. Figure 2 illustrates changes in intensity of υ_4 deformation vibrations of the NH_4^+ ion near 1 400 cm^{-1} in the IR spectra of NH_4-saturated montmorillonite upon heating. The υ_4 NH_4^+ deformation band in the spectra of smectites is the most convenient band to use for quantification purposes, *i.e.*, to quantify the amount of ammonium[20] or to measure the layer charge[21,22]. Two different bands were reported to occur in the IR spectra of

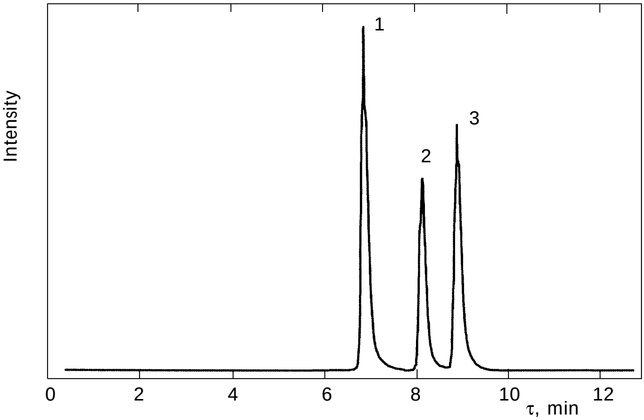


FIG. 1
HPLC analysis of the reaction mixture of catalysed conversion of 3,4,5-trimethoxybenzaldehyde (2) to (3,4,5-trimethoxyphenyl)methylene diacetate (3) with acetic anhydride (1)

NH_4-saturated smectites in the 1 300–1 500 cm^{-1} region, when recorded in KBr pellets. The band near 1 400 cm^{-1} is related to the NH_4Br formed by replacement of NH_4^+ in the mineral with K^+ from KBr, while the band near 1 440 cm^{-1} is assigned to vibrations of NH_4^+ ions present in the interlayers and hydrogen-bonded to oxygen atoms of the clay mineral. This band also appears in the DRIFTS spectra obtained without KBr (ref.[22]). Figure 2 shows that the band near 1 400 cm^{-1} is more intense in this series and that its intensity decreases with the increasing temperature of heating. This is in accord with the expected removal of NH_3 upon heating. Very low absorption at 1 400 cm^{-1} in the spectra of samples heated at ≥500 °C proves that most of ammonium ions were decomposed during the heat treatment. Two components near 1 400 and 1 440 cm^{-1} show that a part of NH_4^+ ions substituted K^+ in KBr but another part got trapped in smectite heated at 300 °C (ref.[23]). This temperature is too low for NH_4^+ decomposition but high enough to cause dehydration and thus collapse of the interlayer spaces, which causes stabilisation of NH_4-smectite to ion exchange with KBr. Gradual collapse of the interlayers was proved by X-ray diffraction (Fig. 3), showing that d_{001} of the samples heated at 500 and 600 °C shrank close to 9.6 Å, *i.e.* to the thickness of the montmorillonite layers[24].

Comparison of DTA curves of Ca- and NH_4-montmorillonites is shown in Fig. 4. Both samples lost water upon heating. The main endothermic peak on the DTA curve of the Ca-form, centered at 84 °C, contains a component

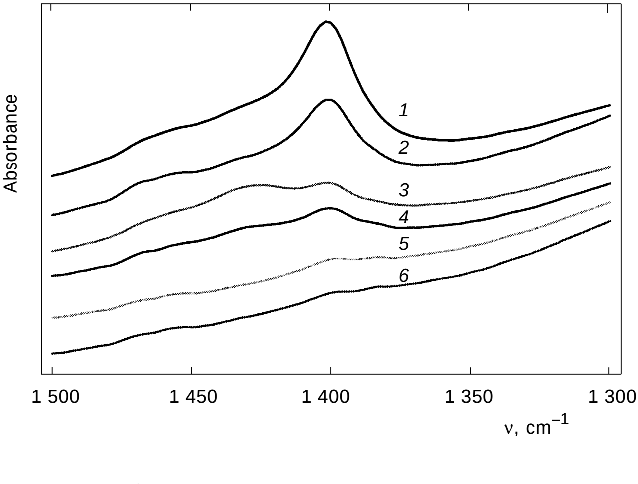


FIG. 2

IR spectra (1 300–1 500 cm^{-1} region) of NH_4-saturated montmorillonite unheated (*1*) and heated at 200–600 °C for 24 h (*2*–*6*) near 170 °C, which is due to removal of water molecules from the inner hydration shells of the Ca^{2+} cations. As expected, this component is absent from the curve of NH_4-montmorillonite. On the other hand, loss of ammonia upon heating is observed near 315 °C.

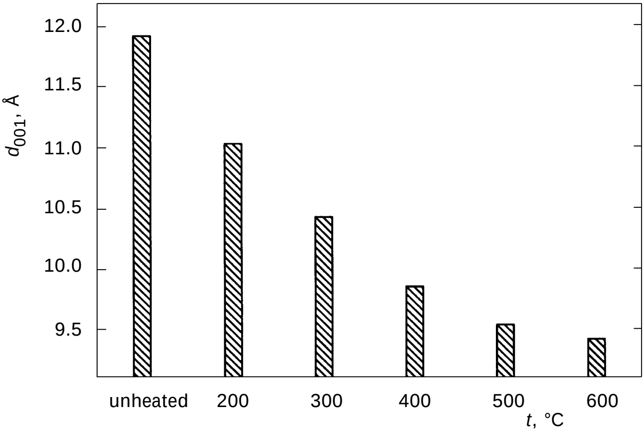


FIG. 3
Decreasing d_{001} values of NH_4-saturated montmorillonite unheated and heated at various temperatures for 24 h

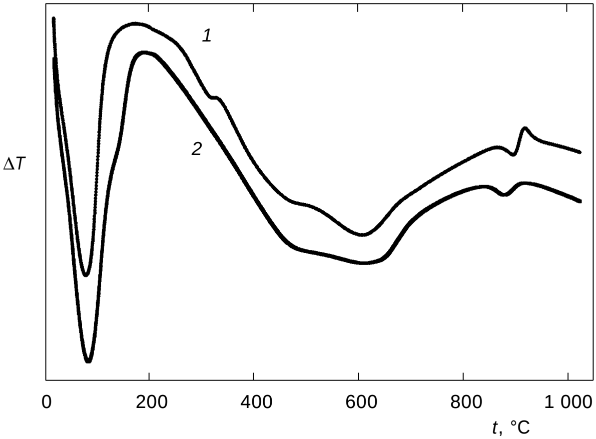
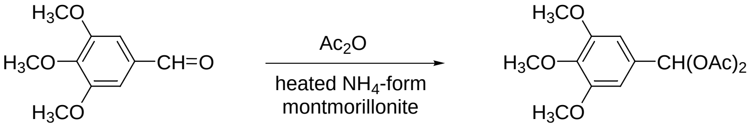


FIG. 4
DTA curves of NH_4- (*1*) and Ca- (*2*) montmorillonites

Catalytic activity of the prepared materials was tested in the reaction of preparation of (3,4,5-trimethoxyphenyl)methylene diacetate from 3,4,5-trimethoxybenzaldehyde (Scheme 1). In the reaction, the aldehyde group is activated by the acid centers present on the catalyst, followed by a nucleophilic attack of the acetanhydride molecule. This reaction is considered to be a suitable alternative for preparation of 1,1-diacetates from aldehydes, with the advantage of selectivity, operational simplicity, high yields, short reaction times and minimal environmental impact[19]. The advantages for the tests of catalysts include high stability of reaction products and their relatively easy and simple analysis, as well as sensitivity to the presence of weak acid sites in the catalysts. Therefore, it is a suitable reaction for testing catalytic activity of differently modified smectites. The results of catalytic tests are shown in Figs 5 and 6.



SCHEME 1

Both unheated forms are of rather low catalytic activity. For the NH_4-form, heating up to 300 °C results in a substantially increased catalytic ac-

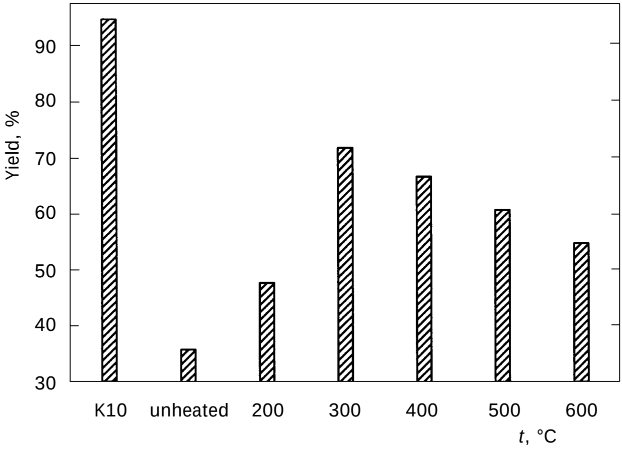


FIG. 5
Yield of diacetate over ammonium-saturated montmorillonite heated at various temperatures for aldehyde protection for 24 h

tivity, though not fully approaching the activity of a commercial acid-activated montmorillonite catalysts K10 (Fig. 5) and KSF (same as K10, not shown in Fig. 5). The increased activity is due to the formation of protons in the course of decomposition of NH_4^+ cations. The protons contribute substantially to the catalytic activity of NH_4-saturated catalysts heated at ≥300 °C. They can also partly attack the layers of montmorillonite, causing partial liberation of structural cations (Al^{3+}, Mg^{2+}, Fe^{3+}) and thus unavailability of protons for catalysis. This is similar to autotransformation, which is known to occur in aqueous dispersions of H-smectites[8]. However, the consequence of autotransformation is complete absence of strong acid sites[25], while the results shown in Fig. 5 prove high catalytic activity (yields > 50%) for all catalysts prepared at ≥300 °C, though the yield of the reaction gradually decreases with increasing temperature of the catalyst preparation. It is assumed that this decrease is due to a decreased number of catalytically active sites present after heating at higher temperatures.

The kinetics of conversion of the aromatic aldehyde in reactions catalysed with K10 and NH_4-saturated montmorillonite heated at 300 °C for 24 h are shown in Fig. 6. Both catalysts are highly effective. Under the conditions used, the reaction catalysed with K10 is clearly faster, reaching 90% yield within about 7 h, while the application of the heated NH_4-clay results in about 70% conversion after 11 h.

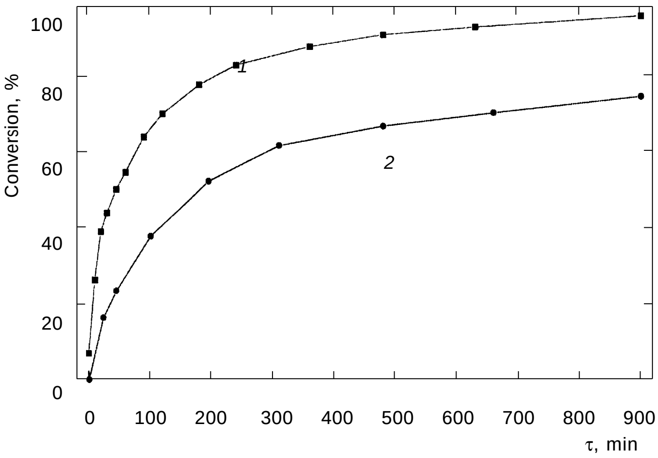


FIG. 6
Comparison of conversions of 3,4,5-trimethoxybenzaldehyde obtained with K10 and ammonium-saturated montmorillonite heated at 300 °C for 24 h

CONCLUSIONS

Active acid catalysts can be prepared by thermal decomposition of NH_4-saturated montmorillonite at 200–600 °C for 24 h. Acetylation of 3,4,5-trimethoxybenzaldehyde with acetic anhydride is a suitable reaction for testing catalytic activity of modified montmorillonites. Most of the prepared materials catalysed the test reaction and gave product yields > 50%. The most active catalyst obtained after heating at 300 °C was slightly less effective than K10, a well-known commercially available acid-activated montmorillonite.

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REFERENCES

1. Adams J. M.: *Appl. Clay Sci*. **1987**, *2*, 309.
2. Laszlo P.: *Preparative Chemistry Using Supported Reagents*. Academic Press, San Diego 1987.
3. Houndry E., Burt W. F., Pew A. E., Jr., Peters W. A., Jr.: *Nat. Pet. News* **1938**, *48*, 570.
4. Decarreau A.: *Matériaux Argileux*. Societé Francaise de Minéralogie et Cristallographie, Paris 1990.
5. Csicsery S. M.: *Zeolites* **1984**, *4*, 202.
6. Varma R. S.: *Green Chem*. **1999**, 43.
7. Vaccari A.: *Catal. Today* **1998**, *41*, 53.
8. Janek M., Komadel P.: *Geol. Carpathica, Ser. Clays* **1993**, *43*, 59.
9. van Olphen H.: *An Introduction to Clay Colloid Chemistry*. Wiley, New York 1977.
10. Wright A. C., Granquist W. T., Kenedy J. V.: *J. Catal*. **1972**, *25*, 65.
11. Davidtz J. C.: *J. Catal*. **1973**, *43*, 260.
12. Barrer R. M.: *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*. Academic Press, New York 1978.
13. Cornelis A., Gerstmans A., Laszlo P., Mathy A., Zieba I.: *Catal. Lett*. **1990**, *6*, 103.
14. Rhodes C. N., Brown D. R.: *Catal. Lett*. **1994**, *24*, 288.
15. Breen C., Watson R., Madejová J., Komadel P., Klapyta Z.: *Langmuir* **1997**, *13*, 6473.
16. Elsen A., Grobet P., Keung M., Leeman H., Schoonheydt R., Toufar H.: Proceedings of Euroclay ‘95, Leuven 1995.
17. Newman A. C. D.: *The Chemistry of Clays and Clay Minerals*. Longman, London 1987.
18. Balogh M., Laszlo P.: *Organic Chemistry Using Clays*. Springer-Verlag, Berlin 1993.
19. Zhang Z. H., Li T. S., Fu Ch. G.: *J. Chem. Res., Synop*. **1997**, 174.
20. Lindgreen H.: *Clay Miner*. **1994**, *29*, 527.
21. Petit S., Righi D., Madejová J., Decarreau A.: *Clay Miner*. **1998**, *33*, 579.
22. Petit S., Righi D., Madejová J., Decarreau A.: *Clay Miner*. **1999**, *34*, 543.
23. Russell J. D., White J. L.: *Clays Clay Miner*. **1966**, *14*, 181.
24. White E. W., McKinstry H. A., Bates T. F.: *Advances in X-Ray Analysis*. Plenum Press, New York 1960.
25. Komadel P., Janek M., Madejová J., Weekes A., Breen C.: *J. Chem. Soc., Faraday Trans*. **1997**, *93*, 4207.