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INCORPORATION OF Fe IN THE INTERLAYER OF Na-BENTONITE *VIA* TREATMENT WITH $FeCl_3$ IN ACETONE

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Abstract—The effect of $FeCl_3$ in acetonic medium on the structure of Na-bentonite was studied using X-ray diffraction (XRD), ^{57}Fe Mössbauer spectroscopy, X-ray fluorescence spectroscopy and infrared spectroscopy to describe the structure of the bentonite before and after treatment. In the samples treated with $FeCl_3$, an increase in the basal spacing was found by XRD, while a new magnetically split component assigned to Fe^{3+} incorporated within the interlayer regions of montmorillonite showed up in the low-temperature Mössbauer spectra. The Mössbauer parameters observed were close to those of Fe oxyhydroxides, suggesting the presence of some kind of nanoparticles. These results show that the treatment with acetonic $FeCl_3$ solution is an effective method for introducing Fe into montmorillonite in the form of Fe^{3+} accommodated in the interlayer region. The treated samples proved to be efficient Lewis catalysts in the acylation of aldehydes (benzaldehyde and 4-OH-benzaldehyde) by acetic acid anhydride.

Key Words—Bentonite, Clay, Interlayer, Iron, Infrared Spectroscopy, Mössbauer Spectroscopy, XRD, XRF.

INTRODUCTION

Cation-exchanged clays can act as catalysts in organic reactions. These reactions are very important in industry (they also occur in nature), because a good yield can be achieved under mild reaction conditions. For example, in our recent paper (Nagy *et al.*, 2002) Zn-montmorillonite catalyzed the formation of 1,1-diacetates from aromatic aldehydes. Li *et al.* (1998) and Zhang *et al.* (1997) reported the preparation of 1,1-diacetates using K10 montmorillonite or Fe^{III}-montmorillonite as catalysts. The preparation of Fe^{III}-montmorillonite (Li *et al.*, 1998) was achieved by impregnation of K10 montmorillonite with a solution of anhydrous $FeCl_3$ in acetone, but as the structure of the catalyst was not examined, it was not known where the Fe^{III} was accommodated.

Naturally, iron can acquire Fe^{II} and Fe^{III} valence states, and both can be present in the structure or in the interlayer space of clays. Reduction of Fe in the structure affects not only the structure of the mineral, but also its properties and reactions (Stucki *et al.*, 2002). When montmorillonite is suspended in an aqueous solution of an Fe salt (either Fe^{II}- or Fe^{III}-salt) in the presence of air, Fe^{III} oxyhydroxides or oxides are formed, at least partially when the starting material was Fe^{II} (*e.g.* Berry *et al.*, 1986; Drame, 2005; Green-Pedersen and Pind, 2000; Izumi *et al.*, 2005; Kong *et al.*, 2005; Kozai *et al.*, 2001; Oliviera *et al.*, 2003; Pálinkó *et al.*, 1996; Pillai and Sahle-Demessie, 2003; Shrigadi *et al.*, 2003). In these papers it was also concluded that the value of the basal spacing, d_{001}, increases if Na(I) is exchanged to Fe^{III} in the interlayer space, and that Fe^{III} is located in an octahedral structure. The formation of Fe oxyhydroxides in the interlayer space has also been suggested (*e.g.* Izumi *et al.*, 2005; Pillai and Sahle-Demessie, 2003).

The formation of 1,1-diacetates from aldehydes and acetic acid anhydride is useful when an aldehyde-protecting group is needed. Usually it is catalyzed by strong proton sources (*e.g.* Aggarwal *et al.*, 1998; Chandra *et al.*, 2000; Deka *et al.*, 1997; Freeman and Karchevski, 1977; Kochhar *et al.*, 1983; Oláh and Mehrotra, 1983, Scriabine, 1961). The reaction had a fairly good yield with various catalysts such as HZSM (Joshi *et al.*, 1993), Y- or β-zeolite (Ballini *et al.*, 1998; Kumar *et al.*, 1995; Pereira *et al.*, 1995), expansive graphite (Jin *et al.*, 1997a, 1997b), N-bromosuccinimide (Karimi *et al.*, 2000), sulfated zirconia (Raju, 1996) and anhydrous ferrous sulfate (Jin *et al.*, 1998).

Our aim was to prepare (like Li *et al.*, 1998) and characterize Fe-exchanged clay. Acetone was used instead of water to minimize the hydrolysis of Fe^{III}. We focused on the change in the structure of the bentonite, on the effect of $FeCl_3$ dissolved in acetone, and on the effect of pure acetone. We investigated whether Fe^{3+} exchanged for Na^+ in the interlayer space, and tested it as a catalyst in the preparation of 1,1-

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diacetates under mild conditions. We used XRD, Mössbauer spectroscopy, X-ray fluorescence (XRF) spectroscopy and infrared (IR) spectroscopy for the characterization of the original Na-bentonite and the ion-exchanged Fe-bentonite.

EXPERIMENTAL

Na-bentonite samples were collected in the Valea Chioarului (Kővár) region of Romania. According to its XRD pattern, the main mineral component is montmorillonite (48%); the other components are cristobalite (25%), K-feldspar (10%), illite (8%), zeolite (4%) and an X-ray amorphous phase (5%). The mineral composition was calculated on the basis of the relative intensity rates of the reflections characteristic of the minerals, applying the literature or experimental corundum factors on minerals (Klug and Alexander, 1954). Elemental analysis of the original Na-bentonite resulted in the following composition: 73.2% SiO_2, 14.2% Al_2O_3, 1.15% Fe_2O_3, 0.82% CaO, 2.24% MgO, 0.4% TiO_2, 2.68% Na_2O, 1% K_2O.

The Na-bentonite was suspended in a solution of anhydrous $FeCl_3$ (Reanal, Hungary) in acetone (Spektrum 3D, Hungary), following the procedure of Li *et al.* (1998); 1.5 g of Na-bentonite and 5 cm^3 acetone were used, the mass of $FeCl_3$ was varied, so that the mass ratio of Na-bentonite to $FeCl_3$ became 1.5:1, 3:1 and 6:1. The solvent was evaporated under reduced pressure.

To study the effect of acetone, 1 g of the starting material was stirred in pure acetone (5 cm^3), then the solvent was evaporated and the clay was also dried in a desiccator.

All treated samples were washed with 1 cm^3 of acetone to remove free salts before analyzing and testing the catalysts. The presence of Fe^{III} in all removed washing solutions was indicated with KSCN reagent. After washing, the samples were dried in a desiccator at room temperature.

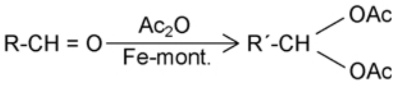
The XRD patterns of the powdered samples before and after treatments were measured by a computer-controlled powder diffractometer (DRON-2) using CoKα radiation (λ = 1.7890) with a β filter. The measurements were carried out at room temperature at a goniometer speed of $1^{\circ}min^{-1}$ in the range of $3-110^{\circ}2\theta$. The XRD patterns were evaluated by the peak-searching computer program 'EXRAY' (Klencsár, 1998).

X-ray fluorescence spectra of all samples were obtained using an energy dispersive X-ray fluorescence system with a radioactive source (^{125}I), a Si(Li) detector with 20 mm^2 surface and 3.5 mm evaporated layer, assisted by a Canberra DSA 1000 digital spectrum analyzer with Canberra Genie 2000 3.0 spectroscopy software.

^{57}Fe Mössbauer spectra of powdered samples were recorded with a conventional Mössbauer spectrometer (Wissel) in transmission geometry at 300 K and 78 K in a temperature-controlled cryostat (Leybold, Germany). Isomer shifts are given relative to α-iron. A $^{57}Co/Rh$ γ-radiation source (3×10^9 Bq activity) was used. The Mössbauer spectra were analyzed by the least-squares fitting of Lorentzian lines with the help of the MOSSWINN code (Klencsár *et al.*, 1996).

The IR spectra of the starting material and treatment with $FeCl_3$ in acetone were recorded using a Perkin Elmer SPECTRUM ONE FTIR spectrometer in the $4000-450$ cm^{-1} region, with 4 cm^{-1} resolution. 2 mg of each sample were powdered with 600 mg of KBr, and 200 mg of this mixture were pressed into a pellet.

The catalytic activity of the $FeCl_3$-treated bentonite on the preparation of 1,1-diacetates from aromatic aldehydes was studied using acetic acid anhydride (Ac_2O). The reaction scheme is as follows:



This reaction was studied on three aromatic aldehydes (benzaldehyde (R = C_6H_5, this group is also denoted by Ph), 4-OH-benzaldehyde (R = 4-OH-C_6H_5), 4-MeO-benzaldehyde (R = 4-CH_3O-C_6H_5) all purchased from Spektrum 3D, Hungary) using Fe-bentonite prepared from Na-bentonite and $FeCl_3$ in a 3:1 ratio. The experiments were also carried out with an α-Fe_2O_3 (Reanal, Hungary) catalyst. A mixture of 0.3 mmol aldehyde, 58 μL (0.6 mmol) Ac_2O, and 5 mg of catalyst (Fe-bentonite or α-Fe_2O_3) was stirred vigorously in 0.5 mL of CH_2Cl_2 as a reaction medium. The end of the catalytic reaction was monitored by thin layer chromatography (TLC) on 10 μL samples taken from the reaction mixture at different reaction times. Precoated silica gel plates (Kieselgel 60F254, 0.25 and 0.5 mm, Merck) and entries: toluene/methanol 9:1, toluene/acetone 20:1 were used; the methanol and acetone were purchased from Spektrum 3D, Hungary and the toluene from Scharlau. The chemicals used were pro anal. quality. When no starting materials were present in the reaction mixture, the catalyst was filtered off and the solvent was evaporated. The product was analyzed by NMR and its melting point was also measured. ^1H NMR spectra were measured with a Brucker Am 360 instrument in DMSO-d_6 (deutero-dimethyl-sulfoxide) with TMS (tetramethylsilane) as the internal standard.

RESULTS AND DISCUSSION

The XRF analysis of the samples showed that the concentration of Fe in the bentonite decreased to nearly half of its original level after the treatment with pure acetone (from 3.4 m/m% to 1.9 m/m%). If the starting material was treated with $FeCl_3$ dissolved in acetone, the amount of Fe increased to 7.07, 9.7 and 12.2 m/m % for bentonite to $FeCl_3$ ratios of 6:1, 3:1 and 1.5:1, respectively.

Due to the XRD pattern of the original Na-bentonite, the lattice parameters of montmorillonite matched other data found in literature for Na-montmorillonite (*e.g.* Kozai *et al.*, 2001). The basal spacing of montmorillonite in the original Na-bentonite was found to be 12.6 Å. Figure 1 shows the XRD pattern of the untreated Na-bentonite (a), that treated with acetone (b), and that treated with $FeCl_3$ in acetone (c).

The treatment with pure acetone did not affect the basal spacing of the montmorillonite, but slight changes in the relative intensity of certain peaks (mainly at 30–32°2θ, related to montmorillonite reflections) occurred. This may be connected with small changes (some degradation) in the structure of the montmorillonite, *i.e.* acetone may have caused the dissolution of some Fe from the montmorillonite. This is shown by the decrease in Fe concentration demonstrated by XRF. Fe^{III} leached from the Na-bentonite was also detected by KSCN reagent in the removed washing solution. The broadening of the 001 peak of the montmorillonite also suggests some structural destruction. The reduction of Fe content in montmorillonite may be a consequence of a partial destruction of the mineral structure. Changes similar to those which we have observed between the XRD patterns were also found by Vlasova *et al*. (2003), when bentonite was dehydrated by an acidic treatment. Those were associated with the destruction of Si–O–Al bonds and with an increase in the number of Si–O bonds due to the destruction of montmorillonite.

When Na-bentonite was treated with $FeCl_3$ dissolved in acetone, the XRD pattern changed in the following way: the basal spacing increased to 16 Å due to incorporation of Fe^{3+} ions into the interlayer space (similar to *e.g.* Izumi *et al.*, 2005; Kong *et al.*, 2005). The relative intensity of the main peaks did not change after this treatment, indicating no change, as observed for acetone only in the structure of the montmorillonite. When bentonite was treated with $FeCl_3$ in acetone at different bentonite to $FeCl_3$ ratios, XRD patterns were found to be very similar to each other. Other changes (besides those corresponding to the incorporation of Fe^{3+} ions into the interlayer space) between the XRD patterns of the original Na-bentonite and of $FeCl_3$-acetone-treated Na-bentonite were examined carefully especially looking for free salts, mainly for $FeCl_3$, in the treated sample, but no free salts or any related compounds could be identified.

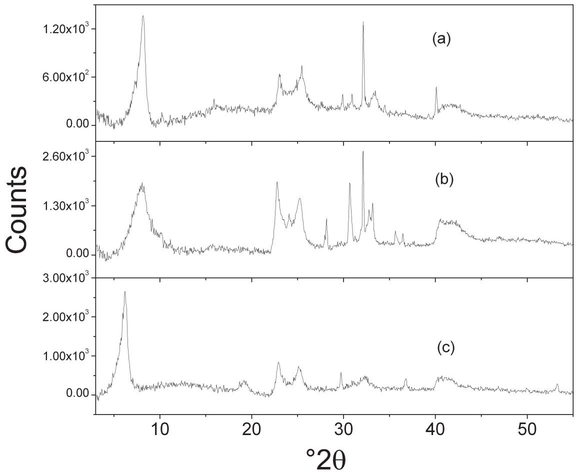


Figure 1. XRD patterns of bentonite from Valea Chioarului (a); after treatment with acetone (b); and after treatment with acetone with $FeCl_3$ (c).

Typical room-temperature Mössbauer spectra of bentonite from Valea Chioarului are shown in Figure 2 for the original sample as well as for those after treatment with either acetone or $FeCl_3$ in acetone. Three main peaks can be recognized on the envelope of these spectra in the 0 to 2.5 mm/s velocity range. The spectra were decomposed into two doublets. The corresponding Mössbauer parameters are given in Table 1. The Mössbauer parameters such as isomer shift, quadrupole splitting,

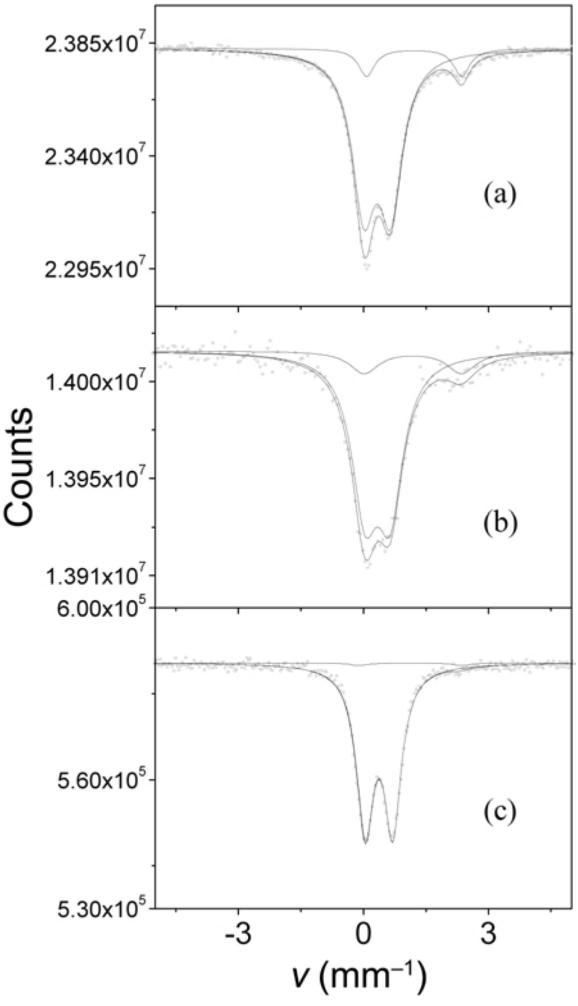


Figure 2. ^{57}Fe Mössbauer spectra of bentonite from Valea Chioarului (a); after treatment with acetone (b); and after treatment of acetone with $FeCl_3$ (c).

Table 1. Mössbauer parameters of bentonites.

Sample	Na-bentonite	Na-bentonite	Na-bentonite treated with acetone	Na-bentonite treated with $FeCl_3$ in acetone 1.5:1	Na-bentonite treated with $FeCl_3$ in acetone 3:1	Na-bentonite treated with $FeCl_3$ in acetone 6:1	Na-bentonite treated with $FeCl_3$ in acetone 3:1
T (K)	293	88	293	293	293	293	74
δ_1 (mms^{-1})	0.34	0.44	0.34	0.35	0.36	0.36	0.47
Δ_1 (mms^{-1})	0.64	0.70	0.63	0.63	0.66	0.69	0.53
A_1 (%)	88.4	89.7	87.0	96.7	97.3	97.8	26.3
δ_2 (mms^{-1})	1.21	1.34	1.20	1.23	1.22	1.24	1.40
Δ_2 (mms^{-1})	2.28	2.35	2.31	2.31	2.32	2.31	2.41
A_2 (%)	11.6	10.3	13.0	3.3	2.7	2.2	2.7
δ_3 (mms^{-1})							0.48
B_3 (T)							41
A_3 (%)							32.1
δ_4 (mms^{-1})							0.47
B_4 (T)							46
A_4 (%)							37.9

δ denotes the isomer shift, Δ denotes the quadrupole splitting, B is the magnetic induction, and A denotes the relative spectral area. The indices 1, 2, 3 and 4 are related to the spectral components of the Fe^{3+} doublet, the Fe^{2+} doublet and two Fe^{3+} sextets, respectively.

magnetic splitting and spectral area give general information about the local electronic density, electric field gradient, magnetic field and vibrational state. These parameters are used here as fingerprints for analytical purposes to distinguish and identify the different Fe microenvironments (Kuzmann *et al*., 1998). The isomer shift and quadrupole splitting values obtained for the original Na-bentonite correspond well with those found earlier for montmorillonites (Stevens *et al*., 1983). δ_1 and Δ_1 values exhibit Fe^{3+} while values of δ_2 and Δ_2 reveal Fe^{2+} microenvironments.

These parameters are typical of octahedrally coordinated Fe^{3+} and Fe^{2+} ions in the structures of silicates (Kuzmann *et al*., 1998; Stevens, 1958–2002). The relative area of the spectral components indicates that the occurrence of the Fe^{3+} species is dominant, as is usually the case for Na-bentonites (Stevens *et al*., 1983). Only regular, temperature-dependent changes of the Mössbauer parameters were observed in the spectrum of the original bentonite recorded at the temperature of liquid nitrogen; no magnetically split components were present.

We have found no significant changes in the Mössbauer spectrum (Figure 2b, Table 1) after treatment with acetone. This treatment did not change the Fe^{2+}/Fe^{3+} ratio significantly as compared to that of the original Na-bentonite. This finding corresponds well with our XRD results which show no change in the lattice parameters of montmorillonite treated with acetone only.

The room-temperature Mössbauer spectra of the samples treated with acetonic $FeCl_3$ solution, however, exhibit changes as compared to the original Na-bentonite. The most significant change in the spectrum is a considerable decrease in the relative occurrence of the Fe^{2+} subspectrum. This indicates that the treatment with $FeCl_3$ in acetone has evidently changed the Fe^{2+}/Fe^{3+} ratio. At the same time, a correlation was found between the change in the relative occurrence of Fe^{2+} and the Fe content of the samples. Consequently, the decrease in the Fe^{2+}/Fe^{3+} ratio upon treatment with $FeCl_3$ in acetone can be attributed to the high uptake of Fe^{3+} by the samples. The Mössbauer pattern of Fe^{3+} microenvironments, freshly introduced by the treatment, can hardly be distinguished from those in the original montmorillonite on the basis of the room-temperature Mössbauer spectra. However, the Mössbauer spectrum of the treated samples recorded at around the temperature of liquid nitrogen showed significant changes (Figure 3) as compared to the original montmorillonite. New magnetically split subspectra, two sextets, have appeared at around the temperature of liquid nitrogen. The Mössbauer parameters of the sextets (Table 1) are similar to those assigned to Fe^{3+} species intercalated between the layers in Fe-exchanged montmorillonite clays by Berry *et al.* (1986). Accordingly, the sextets appearing in our samples can be associated with two main different microenvironments of Fe^{3+} incorporated within the interlayer regions of the montmorillonite structure. The relative areas of the corresponding subspectra (Table 1) indicate that the Fe introduced by the treatment occurs dominantly in these microenvironments. Consequently, our results show that the treatment with acetonic $FeCl_3$ is successful at introducing Fe into the montmorillonite as Fe^{3+} ions in the interlayer region. This is strongly supported by the concomitant increase in the basal spacing as indicated by the XRD results as well as by the catalytic activity of the treated samples. As the Mössbauer parameters of Fe^{3+} in the interlayer are close to those characteristic of Fe^{3+} microenvironments in

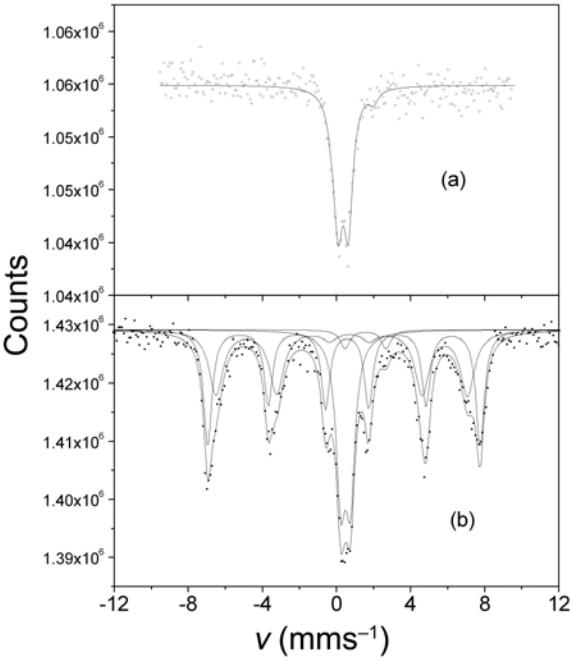


Figure 3. Mössbauer spectra of bentonite before (a) and after (b) its treatment with $FeCl_3$ in acetone, recorded at 74 K.

oxyhydroxides, this may indicate that the ligand environment of Fe^{3+} in the interlayer is somewhat similar to that in the Fe oxyhydroxides. On the other hand, the presence of α-Fe_2O_3 (the catalytic activity of which is found to be close to our Fe^{3+}-treated bentonite) in the samples can be excluded based on the Mössbauer measurements.

Figure 4 shows the IR spectra of the original Na-bentonite and Fe-bentonite (the ratio of bentonite to $FeCl_3$ during the preparation was 3:1). The IR spectrum of the starting material shows typical bands for montmorillonites. When the Na-bentonite is treated with $FeCl_3$ in acetone, the bands characteristic of montmorillonite (*e.g.* Si−O stretching near 1040 cm^{-1}, H−O−H bending near 1630 cm^{-1} and OH-stretching in the range 3400−3600 cm^{-1}) remain the same. This suggests that the structure of montmorillonite did not change during the treatment of Na-bentonite with $FeCl_3$ dissolved in acetone. In the case of treatment with acetonic $FeCl_3$, the intensities of the bands near 3640 and 1630 cm^{-1} characteristic of the stretching and bending of H−O−H decrease. This may be associated with the dehydration of montmorillonite. At the same time, the absorption band due to Si−O bending vibrations at 520 cm^{-1} shifts to a higher frequency and its intensity decreases; in addition, a new absorption band at 775 cm^{-1} due to a dehydroxylated phase is observed. Furthermore, the OH-bending absorption bands (840−940 cm^{-1}) are less intense and a broad shoulder appears between 1070 and 1150 cm^{-1}. Infrared spectroscopy results very similar to ours were found by Bray and Redfern (2000) associated with dehydration and dehydroxylation of montmorillonite.

As the Fe content in the $FeCl_3$-treated samples is greater than the CEC value of the original Na-bentonite, one can expect that, besides the Fe intercalated into the interlayer space, some excess Fe-salt can remain outside or on the surface of the clay. Although our investigating methods were not able to determine that, it can not be entirely ruled out that a minute amount of nano-sized Fe-oxyhydroxide could remain on the surface of the Fe-treated clay.

The catalytic activity of bentonite treated with $FeCl_3$ in acetone was studied in the acylation reaction of aromatic aldehydes. These reactions were also carried out in the presence of α-Fe_2O_3 as a catalyst. The reaction with benzaldehyde and 4-OH-benzaldehyde could be catalyzed by Fe-bentonite just as with α-Fe_2O_3, although the Fe-bentonite did not contain α-Fe_2O_3 according to the Mössbauer studies. Here, the goal was only to show that the acylation reaction can be successfully completed in the presence of catalysts, especially in the case of acetonic $FeCl_3$-treated bentonite, without giving a complete conventional characterization of the kinetics

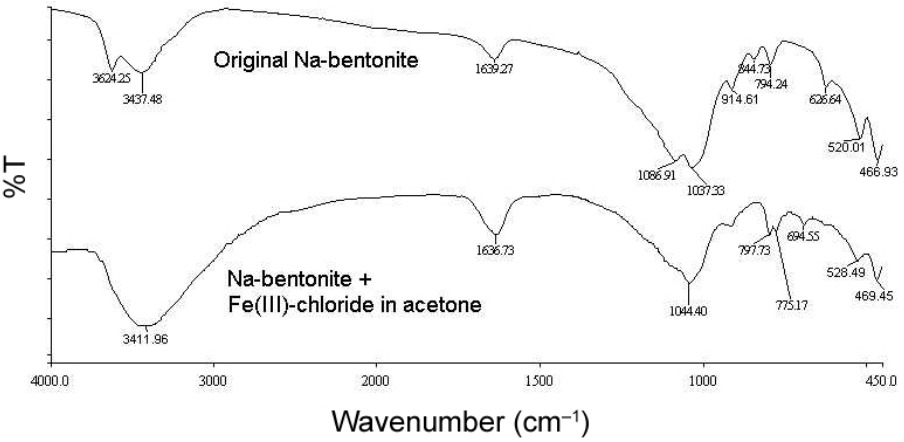


Figure 4. IR spectra of the original Na-bentonite and after the treatment with $FeCl_3$ in acetone.

Table 2. 1,1-diacetates prepared from aromatic aldehydes.

Substrate *R*	Product *R′*	Catalyst	Time	Conversion (%)	M.P. (ºC)		^1H NMR δ (ppm)
					Observed	Reported	
Ph	Ph	Bentonite treated with $FeCl_3$ in acetone	10 min	99	43–43.5	43–45[a]	7.53
Ph	Ph	Fe_2O_3	10 min	99	43–43.5	43–45[a]	7.53
Ph	Ph	Zn-mont.	1 day	99	43–43.5	43–45[a]	7.53
4-HOC_6H_4	4-$AcOC_6H_4$	Bentonite treated with $FeCl_3$ in acetone	2 days	99	89–90	93–95[b]	7.53
4-HOC_6H_4	4-$AcOC_6H_4$	Fe_2O_3	2 days	99	89–90	93–95[b]	7.53
4-HOC_6H_4	4-$AcOC_6H_4$	Zn-mont.	3.5 days	99	89–90	93–95[b]	7.53

[a] Gregory (1970); [b] Bathia *et al.* (1993), *R* denotes the aldehyde group in the substrate (where Ph = C_6H_5), *R′* is the group in the product, the time is required for 99% conversion, M.P. is the melting point and δ denotes the NMR chemical shift.

of catalytic reactions. Therefore the time taken for 99% conversion (monitored by TLC measurement) was used for the characterization, as in the work by Nagy *et al.* (2002), while the melting point as well as NMR chemical shift (δ) characteristic of acetal H identify the end product of the reaction (Table 2). If one compares these conversions of aldehydes into acylals with the data published by Li *et al.* (1998), it can be seen that they also achieved 98% yield within 10 min for benzaldehyde. When the reactant was 4-OH-benzaldehyde, they reached 39% yield within 480 min. As we achieved 99% yield within 2 days, this is similar to what Li *et al.* (1998) found. Our findings were also compared to experiments using Zn-montmorillonite catalysts (Nagy *et al.*, 2002), and it can be seen that the latter are much slower than those reported here. It was found that 4-MeO-benzaldehyde did not react in the presence of any of the catalysts, under these conditions. This can be explained by taking into consideration that montmorillonites act as Lewis acids in the acylation reactions, and a transitional complex may be formed through the oxygen of the aldehyde group. Comparing the cases of 4-OH-benzaldehyde and 4-MeO-benzaldehyde, the methyl group of the latter acts as an electron donor and reduces the electron-accepting ability of the carbon atom of the aldehyde group, which is obviously crucial for the reaction with Ac_2O. Therefore the acylation reaction is expected to be much slower.

After filtering, the investigated clay catalysts can be repeatedly used in acylation reactions.

CONCLUSIONS

Preparing Fe-montmorillonite by reacting montmorillonite with $FeCl_3$ in acetone was successful. According to the XRD patterns, the basal spacing of the montmorillonite increased, therefore Fe^{III} could be introduced into the interlayer space. This is consistent with the Mössbauer spectroscopy measurements. The Mössbauer parameters at liquid nitrogen temperatures are close to that of Fe oxyhydroxides, indicating that some kind of nanoparticles may be present in the interlayer space of the bentonite. It was also found that except for the increasing basal spacing, the treatment with $FeCl_3$ in acetone did not change the structure of the montmorillonite. Fe-bentonite can be used as an efficient catalyst in preparation of 1,1-diacetates from aromatic aldehydes just like α-Fe_2O_3, although the presence of α-Fe_2O_3 is excluded on the basis of the Mössbauer results.

The effect of pure acetone on the structure of the original bentonite is not yet fully understood. The concentration of Fe decreased according to XRF analysis and the Fe^{II}/Fe^{III} ratio increased according to Mössbauer spectroscopy. The XRD patterns showed broadened lines of montmorillonite with smaller intensities and this may be explained by partial degradation of the structure of montmorillonite.

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REFERENCES

Aggarwal, V.K., Fonquerna, S. and Vennal, G.P. (1998) Scandium triflate, an efficient catalyst for formation and deprotection of geminal diacetates (acylals). Chemoselective protection of aldehydes in presence of ketones. *Synlett*, 849–850.

Ballini, R., Bordoni, M., Gosica, G., Maggi, R. and Sartori, G. (1998) Solvent free synthesis and deprotection of 1,1-diacetates over a commercially available zeolite Y as a reusable catalyst. *Tetrahedron Letters*, **39**, 7587–7590.

Bathia, B., Punniyamurthy, T. and Iqbal, J. (1993) Cobalt(II)-catalyzed reaction of aldehydes with acetic anhydride under an oxygen atmosphere: scope and mechanism. *Journal of Organic Chemistry*, **58**, 5518–5523.

Berry, F.J., Hayes, M.H.B. and Jones, S.L. (1986) Investigations of intercalation in inorganic solids with layered structures: Iron-57 Mössbauer spectroscopy studies of size fractionated and iron-exchanged montmorillonite clays. *Inorganica Chimica Acta*, **122**, 19–24.

Bray, H.J. and Redfern, S.A.T. (2000) Influence of counterion species on the dehydroxylation of Ca^{2+}-, Mg^{2+}-, Na^{+}- and K^{+}-exchanged Wyoming montmorillonite. *Mineralogical Magazine*, **64**, 337–346.

Chandra, K.L., Saravanan, P. and Singh, V.K. (2000) An efficient method for diacetylation of aldehydes. *Synlett*, 359–360.

Deka, N., Kalita, D.J., Borah, R.T. and Sarma, J.C. (1997) Iodine as acetylation catalyst in the preparation of 1,1-diacetates from aldehydes. *Journal of Organic Chemistry*, **62**, 1563–1564.

Drame, H. (2005) Cation exchange and pillaring of smectites by aqueous Fe nitrate solutions. *Clays and Clay Minerals*, **53**, 335–347.

Freeman, F. and Karchevski, E.M. (1977) Preparation and spectral properties of benzylidene diacetates. *Journal of Chemical Engineering Data*, **22**, 355–357.

Green-Pedersen, H. and Pind, N. (2000) Preparation, characterization, and sorption properties for Ni^{II} of iron oxyhydroxide-montmorillonite. *Colloids and Surfaces A. Physicochemical and Engineering Aspects*, **168**, 133–145.

Gregory, M.J. (1970) Evidence for a cyclic $A_{A1}1$ mechanism in the hydrolysis of benzilidene diacetates. *Journal of Chemistry Society B*, 1201–1207.

Izumi, Y., Masih, D., Aika, K. and Seida, Y. (2005) Characterization of intercalated iron(III) nanoparticles and oxidative adsorption of arsenite on them monitored by X-ray absorption fine structure combined with fluorescence spectrometry. *Journal of Physical Chemistry B*, **109**, 3227–3232.

Jin, T.-S., Du, G.-Y., Zhang, Z.-H. and Li, T.-S. (1997a) An efficient and convenient procedure for preparation of 1,1-diacetates from aldehydes catalyzed by expansive graphite. *Synthetic Communications*, **27**, 2261–2266.

Jin, T.-S., Ma, Y.-R., Zhang, Z.-H. and Li, T.-S. (1997b) An efficient and facile procedure for deprotection of 1,1-diacetates catalyzed by expansive graphite. *Synthetic Communications*, **27**, 3379–3383.

Jin, T.-S., Ma, Y.-R., Zhang, Z.-H. and Li, T.-S. (1998) An efficient and facile procedure for deprotection of 1,1-diacetates using anhydrous ferrous sulfate. *Organic Preparations and Procedures International*, **30**, 463–466.

Joshi, M.V., Narasimhari, C.S. and Mukesh, O. (1993) Facile conversion of aldehydes to 1,1-diacetates catalyzed by H ZSM-5 and tungstosilicic acid. *Journal of Catalysis*, **141**, 308–310.

Karimi, B., Seradj, H. and Ebrahimian, G.R. (2000) Mild and efficient conversion of aldehydes to 1,1-diacetates catalyzed with N-bromosuccinimide (NBS). *Synlett*, **5**, 623–624.

Klencsár, Z. (1998) '*EXRAY' peak searching computer program*. Personal communication.

Klencsár, Z., Kuzmann, E. and Vértes, A. (1996) User-friendly software for Mössbauer spectrum analysis. *Journal of Radioanalytical and Nuclear Chemistry*, **210**, 105–118.

Kochhar, K.S., Bal, B.S., Deshpande, R.P., Rajadhyaksha, S.N. and Pinnick, H.W. (1983) Conversion of aldehydes into geminal diacetates. *Journal of Organic Chemistry*, **48**, 1765–1767.

Kong, Q., Hu, Y., Lu, H., Chen, Z. and Fan, W. (2005) Synthesis and properties of polystyrene/Fe-montmorillonite nanocomposites using synthetic Fe-montmorillonite by bulk polymerization. *Journal of Materials Science*, **40**, 4505–4509.

Kozai, N., Adachi, Y., Kawamura, S., Inada, K., Kozaki, T., Sato, S., Ohashi, H., Ohnuki, T. and Banba, T. (2001) Characterization of Fe-montmorillonite: A simulant of buffer materials accommodating overpack corrosion product. *Journal of Nuclear Science and Technology*, **38**, 1141–1143.

Klug, H.P. and Alexander, L.E. (1954) *X-ray Diffraction Procedures*. Wiley, New York, London, Paris, 716 pp.

Kumar, P., Hegda, V.R. and Kumar, T.P. (1995) An efficient synthesis of diacetates from aldehydes using beta zeolite. *Tetrahedron Letters*, **36**, 601–602.

Kuzmann, E., Nagy, S., Vértes, A., Weiszburg, T. and Garg, V.K. (1998) Applications of Mössbauer spectroscopy in mineralogy and geology. Pp.285–376 in: *Nuclear Methods in Mineralogy and Geology* (A. Vértes, S. Nagy and K. Süvegh, editors). Plenum, New York.

Li, T.-S., Zhang, Z.-H. and Gao, Y.-J. (1998) A rapid preparation of acylals of aldehydes catalysed by Fe^{3+}-montmorillonite. *Synthetic Communications*, **28**, 4665–4571.

Nagy, N.M., Jakab, M.A., Kónya, J. and Antus, S. (2002) Convenient preparation of 1,1-diacetates from aromatic aldehydes catalysed by zinc-montmorillonite. *Applied Clay Science*, **21**, 213–216.

Oláh, G.A. and Mehrotra, A.K. (1983) Improved Nation-H catalyzed preparation of 1,1-diacetates from aldehydes. *Synthesis*, 962–963.

Oliveira, L.C.A., Rios, R.V.R.A., Fabris, J.D., Sapag, K., Garg, V.K. and Lago, R.M. (2003) Clay-iron oxide magnetic composites for the adsorption of contaminants in water. *Applied Clay Science*, **22**, 169–177.

Pálinkó, I., Lázár, K., Hannus, I. and Kiricsi, I. (1996) Step towards nanoscale Fe moieties: Intercalation of simple and Keggin-type iron-containing ions in between the layers of Na-montmorillonite. *Journal of Physics and Chemistry of Solids*, **57**, 1067–1072.

Pereira, C., Cigante, B., Marcelo-Curto, M.J., Carreyre, H., Perot, G. and Gausnet, M. (1995) Diacetates from aldehydes in the presence of zeolites. *Synthesis*, 1077–1078.

Pillai, U.R. and Sahle-Demessie, E. (2003) Oxidation of alcohols over Fe^{3+}/montmorillonite-K10 using hydrogen peroxide. *Applied Catalysis A: General*, **245**, 103–109.

Raju, S.V.N. (1996) Sulfated zirconia: an efficient catalyst for the synthesis of 1,1-diacetates from aldehydes and ketones. *Journal of Chemical Research (Synopses)*, p. 68.

Scriabine, I. (1961) Nouveau procédé de préparation des aldéhydes dihirocinnamique. *Bulletin Société Chimie de France*, 1194–1198.

Shrigadi, N.B., Shinde, A.B. and Samant, S.D. (2003) Study of catalytic activity of free and K10-supported iron oxyhydroxides and oxides in the Friedel-Crafts benzylation reaction using benzyl chloride/alcohol to understand their role in the catalysis by the Fe-exchanged/impregnated K10 catalysts. *Applied Catalysis A: General*, **252**, 23–25.

Stevens, J.G. (editor) (1958–2002) *Mössbauer Effect Reference and Data Index (MERDI)*. Interscience, New York

Stevens, J.G., Pollak, H., Li, Z., Stevens, V.E., White, R.M. and Gibson, J.L. (editors) (1983) *The Mössbauer Handbook of Minerals E*. Asheville, North Carolina, USA.

Stucki, J.W., Lee, K., Zhang, L. and Larson, R.A. (2002) Effects of iron oxidation state on the surface and structural properties of smectites. *Pure and Applied Chemistry*, **74**, 2145–2158.

Vlasova, M., Dominguez-Patiño, G., Kakazey, N., Dominguez-Patiño, M., Juarez-Romero, D. and Enríquez Méndez, Y. (2003) Structural-phase transformations in bentonite after acid treatment. *Science of Sintering*, **35**, 155–166.

Zhang, Z.-H., Li, T.-S. and Fu, Ch.-G. (1997) An efficient and convenient procedure for preparation of 1,1-diacetates from aldehydes. *Journal of Chemical Research (Synopses)*, 174–175.

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