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Preparation, structural and surface characterization of kaolinite nanocomposites suitable for environmental technological applications

Ph.D. THESES

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Introduction

Nowadays there is a growing need for treating polluted waters in an environmentally friendly way. A possible solution is offered by the use of 1:1 type clay minerals due to their inherent photochemical activity. The currently available photocatalysts are mostly artificially prepared and difficult to recover, making them expensive to use. Clay minerals of natural origin, available in large quantities, may provide an alternative for photochemical decomposition of contaminants; especially in view of the fact that their surface modification can further increase their activity. Many researchers studied this topic, however, the physicochemical background of the factors inducing photochemical activity is not fully discovered yet.

Aims

The aim of this work is to find relationship between the structural - and surface properties of clays and their photochemical activity. I investigated the effect of defect sites - formed by heat treatment of a contaminant-free clay mineral - on the photochemical activity. My goal was to study the physicochemical reasons of photochemical behaviour, since it is questionable whether the usual mechanism based on electron-hole pair recombination is applicable. I also investigated the applicability of an iron-contaminated clay mineral from natural deposits in order to discover the role of structural and mineral contaminants in photochemical activity. My goal was also to study the degradability of more complex, environmentally relevant organic compounds, as well. Finally, I searched for correlations between surface properties and photochemical activity.

Experimental

First of all, I performed heat treatment on a contaminant-free, commercially available halloysite at specified temperatures (400-480°C) and time (30-180 min). The structural changes were followed by means of XRD, ^{27}Al MAS NMR and FTIR techniques. Morphological changes were identified through the changes of the surface area and with TEM analysis. The acid/base character of the structural defect sites was determined with TPD and ^{1}H MAS NMR. The effect of the defect sites was studied with the degradation of oxalic acid. The mechanism of the photodegradation was analysed with the coumarin-test, which can be used to determine the amount of the formed •OH-radicals. The well-crystalized sample was compared to two samples from a natural site with low contamination content.

In order to increase the specific surface area and thus the catalytic activity of high iron content kaolin, exfoliation was made with a four-step intercalation method. The intercalation and exfoliation were monitored by XRD and the change in specific surface area was analysed by N_2 adsorption. The change in photochemical activity was investigated through the degradability of oxalic acid.

Based on the results of the contaminant-free samples, I also modificated the surface of the high iron content clay mineral. In this case, I applied different concentrations (1-3 M) of HCl for a certain period of time (1-6 h) to optimize the amount of iron content and to create reduced Al-coordinations. The changes in the structure were monitored by XRD method. The morphological changes were examined by determining the specific surface area and the element distribution by analysing TEM and EDX images. Defect sites caused by surface modification were monitored by ^{27}Al MAS NMR spectroscopy. I used the TPD method to study the acid/base character of the surface. Photochemical activity was investigated through the degradability of oxalic acid. For the best performing sample, I used heat treatment (400 ° C, 30 and 180 min) to create additional defect sites.

The study of photochemical activity was extended with the degradability of gas-phase toluene, liquid-phase 4-nitrophenol and methyl orange. The studies were performed as a pre-experimental measurement. The degradability of toluene was monitored by gas-phase FTIR and the photodegradation of 4-nitrophenol and methyl orange by UV-Vis spectrophotometer.

The determination of the surface properties of the prepared catalysts was supplemented by inverse gas chromatography to correlate photochemical activity as well as surface acid-base properties.

Table 1 Summary of sample and the analytical methods used

Samples designation	Description
Exfoliation of kaolinite contaminated with mineral and structural iron	
K	Untreated kaolinite
K-KAc	Kaolinite – potassium-acetate complex
K-EG	Kaolinite – ethylene glycol complex
K-HA	kaolinite – hexylamine complex
K-T	Kaolinite exfoliated with toluene
K-nano	Kaolinite nanostructure, after surface cleaning
Exfoliation of kaolinite contaminated with mineral and structural iron, after acid treatment	
KS	Acid treated kaolinite (11M HCl, 3 h)
KS-KAc	Acid treated kaolinite – potassium-acetate complex
KS-EG	Acid treated kaolinite – ethylene glycol complex
KS-HA	Acid treated kaolinite – hexylamine complex
KS-T	Acid treated kaolinite exfoliated with toluene
KSnano	Acid treated kaolinite nanostructure after surface cleaning with acetone, isopropyl alcohol and MilliQ water
KSnano-H_2O_2	Acid treated kaolinite after surface cleaning with hydrogen-peroxide
Acid treatment of a high iron content kaolinite	
K-X-Y	Acid treated kaolinite X: Acid concentration (11M, 8M, 5M) Y: Treatment time (1, 3, 6 h)
K-X-Y-C	Acid treated kaolinite, examined for 5 cycles
Heat treatment of halloysite samples	
SHNT	Commercially available halloysite
HNT1, HNT2	Raw, natural halloysite samples
HNT1-C	Raw, natural halloysite sample, examined for 5 cycles
SHNT-X-Y	Heat treated halloysite X: Treatment temperature (200 °C, 400 °C, 480 °C) Y: Treatment time (30 min, 45 min, 60 min, 90 min, 105 min, 180 min)
Composites	
SHNT-X-Y-TiO_2	SHNT-TiO_2 composite X: Temperature of preparation Y: Preparation time
SHNT-ZnO-X/ HNT2-ZnO-X	X: Amount of ZnO on the surface of halloysite (2,4%, 4,3%, 8,7%, 15,8%, 27,7%)
Analytical methods	
XRD	X-ray Powder Diffraction
FTIR	Fourier-transform infrared spectroscopy
TG	Thermogravimetry
DTG	Differential thermogravimetry
MAS NMR	Magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy
TPD	Temperature programmed desorption method
TEM	Transmission electron spectroscopy
EDX	Energy dispersive X-Ray analysis
IGC	Inverse gas chromatography

Results

Heat treatment of the well-crystallized, contaminant-free clay mineral resulted in the removal of OH-groups leading to the formation of defect sites in the structure. Based on ^{27}Al MAS NMR results, decreased Al-coordinations appeared, as well. The defect sites increased the surface acidity based on TPD and ^{1}H MAS NMR results; and also raised the oxalic acid degradation efficiency. Interestingly, even a highly dehydroxylated sample has significant photochemical activity. (**Figure 1, SHNT-480-105, 83% dehydroxylation**)

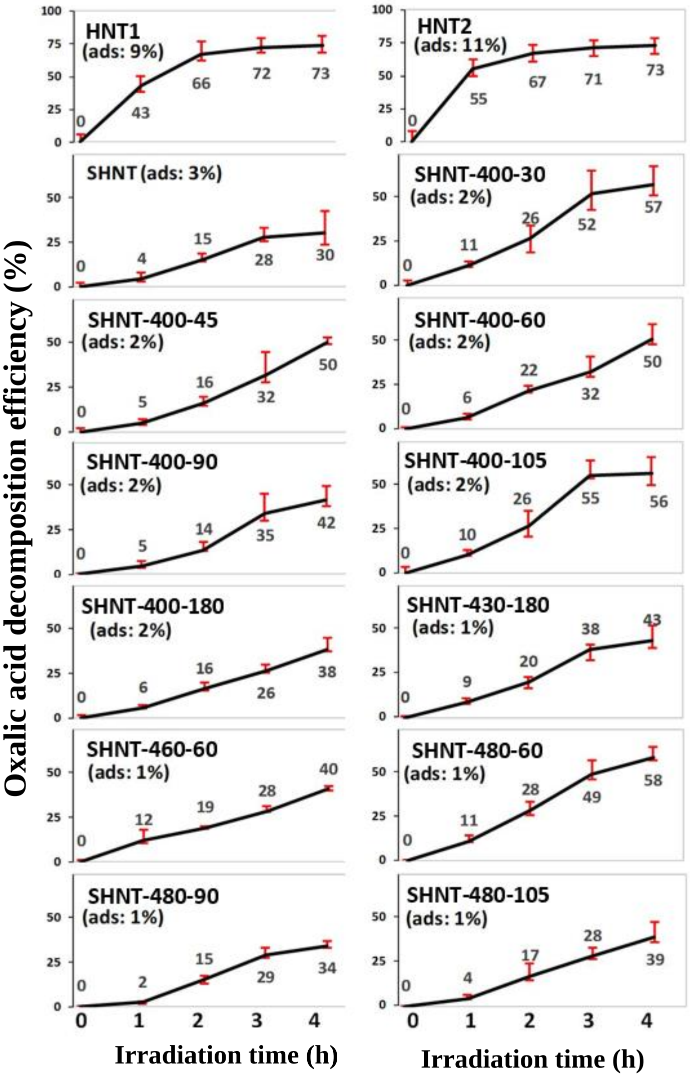

Figure 1. Oxalic acid degradation on HNT1, HNT2 and SHNT samples. Irradiation:1 – 4 h, λ_{max}=365 nm.

Comparing the results of the low-contaminated samples with the commercially available one it can be seen that the higher specific surface area significantly increased the photochemical activity. This is due to the availability of a larger reaction surface. (**Figure 1, HNT11, HNT2 samples**)

I hypothesized the e^-/h^+ pair mechanism among the factors of the photochemical activity of 1:1 type clay minerals. However, based on the coumarin tests, the amount of generated OH radicals cannot be correlated with the oxalic acid degradation efficiency. Therefore, it is believed that the complexing properties of the test compound may underlie the physicochemical background of the activity.

Based on the proof of the significance of the specific surface area, I tried to exfoliate the high structural- and mineral iron content clay mineral. However, the specific surface area of the formed nanostructure did not change and - compared to the initial sample - its photochemical activity decreased. This is presumably due to the presence of structural iron, as the difference in the size of the Fe^{3+} ion replacing the Al^{3+} ion can cause a structural change and prevents the individual TO layers from folding up, thereby promoting rearrangement. There is currently no economic way to prevent reorganization and photoactivity would not reduce as well.

After the failure to increase the specific surface area, I used the results of the contaminant-free clay mineral and I performed further studies with the high iron content clay mineral. The surface modification was performed by acidification, which caused changes only in the surface, based on the XRD results. Low-coordination Al defect sites appeared on the surface/edges. Although the presence of defect sites increased oxalic acid degradation efficiency, reproducibility was achieved for one sample, only. The additional surface modification method created additional defect sites, which further increased the photochemical activity. (**Figure 2.**)

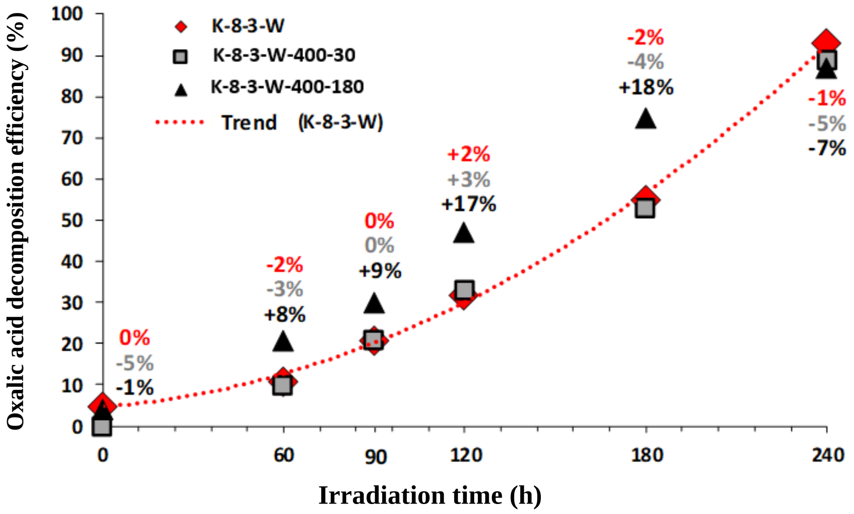

Figure 2. **Kinetics of oxalic acid decomposition for K-8-3-W, and its heat-treated versions. The error of analysis is ± 0,2%.**

Model test compounds with environmental relevance showed that the surface of the catalysts should be designed by functional groups. The energy of the photons was not enough to decompose aromatic groups, there is a need to provide energy in a different way, for example with chemical energy.

While characterising the surface of the clay mineral catalysts with TPD, I found limitations in the measurement procedure. Parallel with the desorption of the test gases, dehydration and dehydroxylation also take place at the temperature used. The TCD detector is not suitable to make difference between the removed water and the test compounds that makes an error in the results. Based on thermal analysis, I determined the pre-treatment temperature at which dehydration takes place, but dehydroxylation does not start yet. Using a pre-treating method at the specified temperature can solve this problem.

Finally, I tried to achieve more detailed results on the surface properties by IGC studies, which can be a complementary technique to TPD and ^{1}H MAS NMR. The results have shown that the inhomogeneity of the surface can form a wide variety of binding sites with different binding energies. The dispersive, specific, as well as the acid-base components of the binding energies and their ratios are closely correlated with catalytic efficiency and reproducibility and a radical-type function. (**Figure 3.**) This relationship may significantly improve the designability of catalysts in the future via optimizing the ratio of dispersive and specific as well as acidic and basic binding sites.

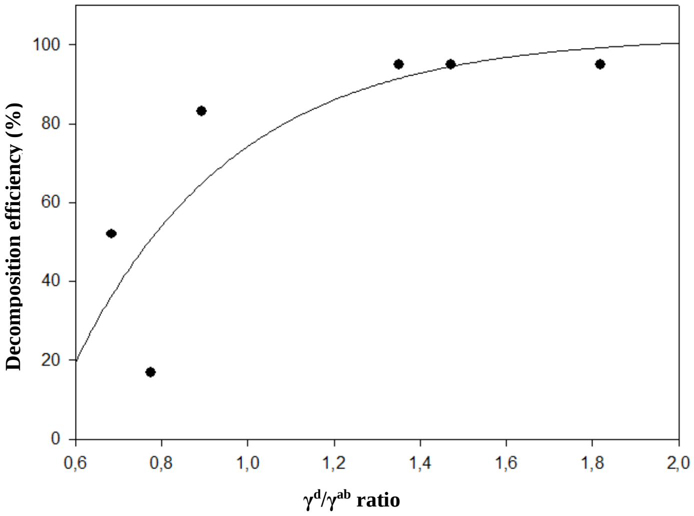

Figure 3. Correlation between the decomposition efficiency and the dispersive/specific component ratio of the tested kaolinite and halloysite samples

Thesis points

I investigated the parameters influencing the photochemical activity of a well-crystallized, contaminant-free clay mineral. I compared its properties with two clays of low contamination.

1.1. Upon heat treatment, OH groups were removed from the surface, forming defect sites with reduced Al coordination. With the increase of the temperature and treatment time first ^{V}Al and then ^{IV}Al coordination appears in increasing amounts, leading to the formation of acidic binding sites at the surface based on TPD and ^{1}H MAS NMR results.

1.2. Photochemical activity increases upon heat treatment. Interestingly, even in the case of a significant (83%) loss of OH groups and structural degradation, the sample has a higher oxalic acid degradation efficiency compared to the untreated halloysite.

1.3. Investigating the mechanism of photodegradation, •OH radical formation was hypothesized; however, the results did not correlate with oxalic acid degradation efficiency. Thus, the classical semiconductor decomposition mechanism is not applicable in this case. Presumably, the complexing properties of oxalic acid also play a role in the process.

2. To increase the surface area of a high mineral- and structural iron content kaolinite I used a four-step intercalation method to exfoliate the layered structure.

2.1. In case of mineral iron content, the surface area did not increase, exfoliation had a low efficiency (30±5%). The presumed cause is the layer stabilizing effect of the compound formed between the mineral iron and hexylamine.

2.2. The exfoliation procedure was performed even after the removal of the mineral iron content by acidification. The efficiency of exfoliation was also low in this case, the specific surface area significantly reduced. This is mainly due to the presence of structural iron. The Fe^{3+} ion, which replaces the Al^{3+} ion, modified the cell parameters and the individual TO-sheet remained planar.

3. I investigated the possibility of increasing the photochemical activity of natural, high iron content kaolinite.

3.1. The acid treatment created defect sites on the surface, but the structure remained intact. The amount of mineral iron content decreased.

3.2. Interestingly, although the oxalic acid degradation efficiency increased, reproducibility was achieved for one sample, only.

    3.3. With the use of heat treatment on the well-performing sample it can be demonstrated that not only the decrease in iron content but also the change in Al coordination number can enhance the photochemical activity.

4. I investigated whether the mechanism of photochemical activity based on complex formation can be applied to other test compounds and whether the results obtained so far can be applied to other composite systems.
    4.1. The use of photodegradation of methyl orange in the presence of a halloysite-ZnO catalyst as a test method is questionable. The high adsorption capacity made impossible to make a distinction between photodegradation and surface adsorption.
    4.2. Examination of the degradability of 4-nitrophenol and toluene gave partial results. The photochemical activity of the halloysite-ZnO composite was observed, however, the energy of the system was not sufficient for complete mineralization.
    4.3. It may be appropriate to consider the design of clay mineral catalysts by the type of molecules to decomposes.
5. I investigated the surface acid/base properties of the formed catalysts by IGC method.
    5.1. Based on the results, the increase in the basic character of the dispersive component shows a strong correlation with the photochemical activity of the samples. Determining this relationship makes the design of catalysts for a given test substance easier.
    5.2. While ^{1}H MAS NMR studies showed the formation of acidic binding sites as a result of the surface treatment, the IGC method indicated an increase in the photochemical activity with the increase in the basic component ratio.
    5.3. The different results of the two methods are due to the fact that while the ^{1}H MAS NMR method provides information about the entire structure, the IGC provides information on the surface accessible to the molecules. In this interpretation the information content of the two methods is complementary.

Publications related to the topic of the dissertation

Publications

1. Veronika Vágvölgyi, **Katalin Győrfi**, Balázs Zsirka, Erzsébet Horváth, János Kristóf: *The role of thermal analysis in the development of high-iron-content kaolinite-based photocatalysts,* Journal of Thermal Analysis and Calorimetry, 2020, https://doi.org/10.1007/s10973-020-09350-2
2. **Katalin Győrfi**, VeronikaVágvölgyi, Balázs Zsirka, Erzsébet Horváth, Róbert K. Szilágyi, Kornélia Baán, Szabolcs Balogh, János Kristóf: *Kaolins of high iron-content as photocatalysts: Challenges of acidic surface modifications and mechanistic insights,* Applied Clay Science, 2020, https://doi.org/10.1016/j.clay.2020.105722
3. Balázs Zsirka, Veronika Vágvölgyi, **Katalin Győrfi**, Erzsébet Horváth, Róbert K. Szilágyi, Erzsébet Szabo-Bárdos, Szabolcs Balogh, János Kristóf*: Compositional, structural, and surface characterization of heat-treated halloysite samples: Influence of surface treatment on photochemical activity,* Applied Clay Science, 2021, https://doi.org/10.1016/j.clay.2021.106222

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2. **Győrfi Katalin**: *Vastartalmú kaolinit nanostruktúrák előállítása, szerkezeti és fotokémiai tulajdonságainak vizsgálata*, XXXIV. Országos tudományos diákköri konferencia, 2019. március 22.
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4. **Katalin Győrfi**, Balázs Zsirka, Veronika Vágvölgyi, Erzsébet Horváth, János Kristóf: *Exfoliation, surface modification and photocatalytic application of an iron-rich kaolinite,* 2nd Journal of Thermal Analysis and Calorimetry Conference, 2019. június 21.
5. Veronika Vágvölgyi, **Katalin Győrfi**, Balázs Zsirka, Erzsébet Horváth, János Kristóf: *Influence of the modified iron content on the photocatalytic activity of kaolinite,* 2nd Journal of Thermal Analysis and Calorimetry Conference, 2019. június 21.
6. **Győrfi Katalin**, Zsirka Balázs, Vágvölgyi Veronika, Horváth Erzsébet, Kristóf János: *Savazással módosított magas vastartalmú kaolinit szerkezeti és felületi jellemzése, fotokémiai aktivitásának vizsgálata*, Pannon Tudományos Nap, 2019. október 16.
7. **Katalin Győrfi**: *Surface modification of iron rich kaolinite with acid treatment: characterisation of structure and surfaces,* Green Solutions 2019 Conference, 2019. december 11.