

Katarzyna BRÜCKMAN *, Jerzy FIJAŁ **, Jerzy HABER *.
Zenon KŁAPYTA **, Tomasz WILTOWSKI *, Witold ŻABIŃSKI **

INFLUENCE OF DIFFERENT ACTIVATION METHODS ON THE CATALYTIC PROPERTIES OF MONTMORILLONITE

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Abstract. Structure and catalytic properties of natural montmorillonite and products of its activation have been studied. The natural montmorillonite has been activated by HCl, HF, KF and NH_4F solutions. One of the samples was also calcined. Chemical, X-ray diffraction and infrared spectroscopic methods have been applied. Catalytic activity of montmorillonite in cracking of cumene has also been studied using microreactor pulse technique. Samples activated with HCl solution and activated using NH_4F solution and then calcined were found to show high catalytic activity.

INTRODUCTION

Catalytic properties of natural clays, particularly of montmorillonite and its activation products, have been the subject of many studies. It has been found that they show catalytic activity in cracking of cumene (Greenall, Alexander 1948, Mills *et al.* 1950, Milliken *et al.* 1955), polymerization (Solomon, Rosser 1965, Solomon Loft 1967, Solomon *et al.* 1968, Solomon 1968, Theng, Walker 1970), isomerization (Grim 1962) and other reactions, which may be related to acid properties of natural clays and products of their activation (Covini *et al.* 1967a, b, Sato *et al.* 1964, Dzisko 1964). The acid properties are due to the presence of acid centres of Brönsted and Lewis type on the surface of a solid. The Brönsted acid centres are generated by various processes. One of those consists in the introduc-

* Research Laboratories of Catalysis and Surface Chemistry, Cracow (Kraków, ul. Krupnicza 41).

** Academy of Mining and Metallurgy, Institute of Geology and Mineral Deposits, Cracow (Kraków, al. Mickiewicza 30).

tion of H_3O^+ cation in the exchangeable positions of montmorillonite. The acid properties of such montmorillonite increase after its dehydration, which results in the deprotonisation of H_3O^+ ions and migration of released protons to octahedral layer. The protons break Si-O-Al bonds and simultaneously the new bonds Si-OH or Al-OH are created. The jump of protons between the nearest oxygen atoms induce for the moment a change in the charge of adjacent Al or Si atoms (Fripiat 1971). Analogous process may occur as the result of thermal decomposition of ammonium form of montmorillonite or the complex of the mineral with various organic cations. The acid properties of montmorillonite can also be generated by the presence of interlayer water, its degree of dissociation being much greater than that of the water in liquid state.

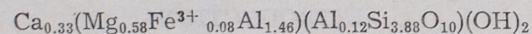
The Si-OH groups localized in the place of discontinuity of the network on the edge of a crystallite constitute also the Brönsted acid sites. The Lewis acid sites appear in the place occupied by Al or Si atoms with excess positive charge. Breaking of Si-O-Al bond by migration of protons to octahedral layer as well as the presence of broken bonds on the edge of crystallites give rise to Lewis acid sites.

Determination of the influence of various methods of activation of montmorillonite on the concentration of acid sites and their catalytic activity in cracking of cumene was the aim of the present study.

EXPERIMENTAL

Material

The montmorillonite separated by sedimentation from miocene bentonite from Chmielnik (Fijałkowska, Fijałkowski 1966) has been used in these investigations. This is a typical dioctahedral montmorillonite, containing Ca^{2+} cations in the exchangeable positions. Its approximate formula is:



Methods of investigation

The samples of montmorillonite were activated using HCl, HF, KF and NH_4F solutions. Sample number 6 was also calcined (Tab. 1). Structural changes of the products of activation were examined by chemical, X-ray and infrared spectroscopic methods. The amount of fluorine was determined by titration with $Th(NO_3)_3$ solution after previous distillation. This part of silica, which was dissolved in 0.5 n solution of Na_2CO_3 , was assumed to be amorphous.

The X-ray analysis was carried out using TUR M-61 diffractometer.

The infrared spectroscopic analysis was carried out by means of UR-10 (Zeiss) spectrophotometer. The samples were prepared in the form of KBr discs.

The surface area was determined from the adsorption isotherm of argon in liquid nitrogen temperature by means of BET-equation.

Cracking of cumene was chosen as the test reaction. Catalytic activity was examined using a microreactor pulse technique. The reaction products were analyzed by gas chromatography with the help of a flame ionization detector (silicone oil column, $150^\circ C$).

RESULTS

Results obtained for the untreated montmorillonite (sample 1) and for the products of its activation (samples 2—6) are presented in tables 1—2 and Figures 1—2.

Table 1
Results of investigation of montmorillonite and products of its activation

Sample number	Mode of preparation of a catalyst	Amorphous silica content (weight %)	Fluorine content (weight %)	Surface area m^2/g
1	Natural montmorillonite (untreated)	7.62	0.00	63.8
2	Montmorillonite activated by HF solution	35.84	8.56	150.0
3	Montmorillonite activated by HCl solution	48.76	0.00	236.2
4	Montmorillonite activated by KF and HCl solutions	18.30	1.35	
5	Montmorillonite activated by KF solution	2.81	17.33	119.0
6	Montmorillonite activated by NH_4F solution and calcined	3.03	3.36	140.0

Surface area of the natural montmorillonite ($63.8 m^2/g$) is typical for this type of minerals. The predominant pore radius is about 15 Å. The great amount of amorphous silica is due to the presence of unaltered volcanic glass. Results of X-ray analysis are presented in Figure 1a and IR spectrum in Figure 2a.

Activation by means of acid solution results in the increased amount of amorphous silica and the rise of surface area (see Table 1). The partial decomposition of crystal lattice induced by elimination of Al and Mg cations from octahedral layer results in the formation of large amount of amorphous silica, as indicated by the decrease of intensity and broadening of basal reflection 001 ($d \approx 15.5 \text{ \AA}$) and in the weakening of the reflections $hk0$. The decrease of intensity of absorption bands corresponding to librations AlAlOH and AlMgOH (930 and 850 cm^{-1} , respectively), of the valence vibrations Al-O (540 cm^{-1}) and the valence vibrations O-H (about 3630 cm^{-1}) may be noticed in the IR absorption spectrum. The

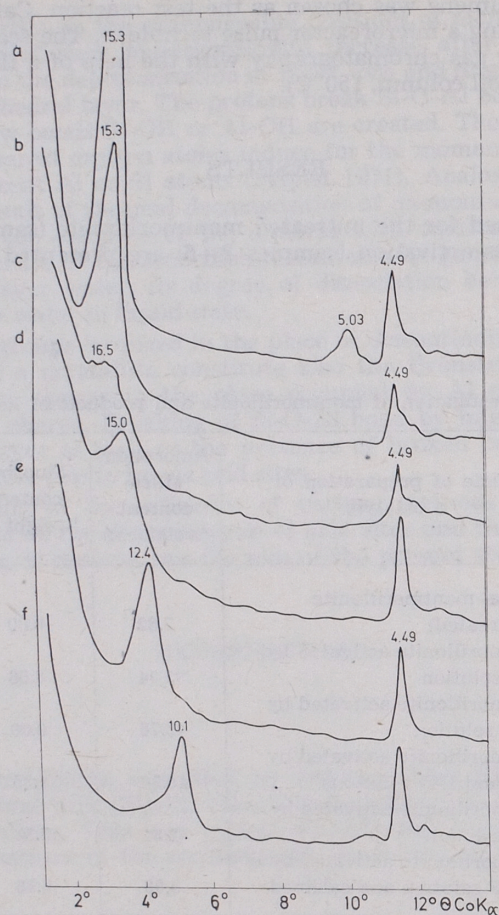


Fig. 1. X-ray diffractograms of the montmorillonite from Chmielnik and products of its activation

a — untreated montmorillonite, b — product of its activation with HF solution, c — product of its activation with HCl solution, d — product of its activation with KF and then HCl solutions, e — product of its activation with KF solution, f — product of its activation with NH_4F solution and subsequent calcination

rise of intensity of the absorption band connected with the creation of secondary amorphous silica gel, with absorption maximum about 800 cm^{-1} (the vibrations Si-O-Si) can also be observed. Moreover, the acid activation results in the broadening of the absorption band due to vibrations ν_3 of SiO_4 tetrahedra in the range of $950\text{--}1250\text{ cm}^{-1}$.

Some differences in the type of products were observed depending on the time of activation and the kind and concentration of acid solution. The activation by the HCl solution (sample 3) results in the maximum amorphization and the greatest surface area. Thus, the considerable

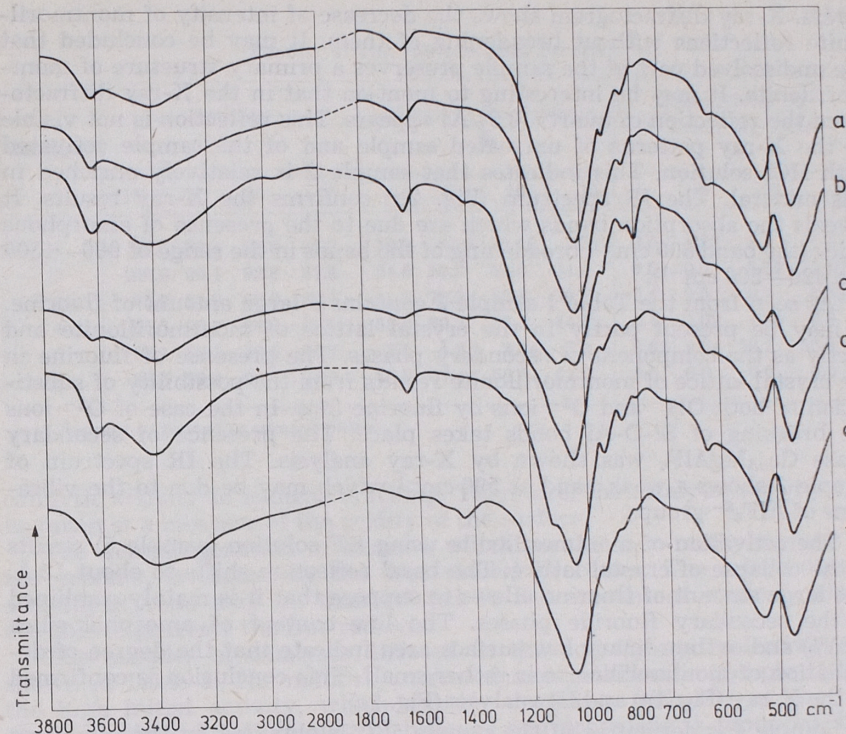


Fig. 2. Infrared absorption spectra of the montmorillonite from Chmielnik and products of its activation

a — untreated montmorillonite, b — product of its activation with HF solution, c — product of its activation with HCl solution, d — product of its activation with KF and then HCl solution, e — product of its activation with KF solution, f — product of its activation with NH_4F solution and subsequent calcination

broadening and weakening of the reflection 001 (about 15.5 \AA) and the decrease of the intensity of the general reflection 110 (4.49 \AA) is observed in X-ray diffractogram (Fig. 1c). The IR absorption of sample 3 (Fig. 2c) resembles the IR spectrum of amorphous silica: the broad absorption band ν_3 in the range of $900\text{--}1200\text{ cm}^{-1}$, the strong Si-O-Si band 800 cm^{-1} and the intensive band with the maxima 470 and 525 cm^{-1} are observed. In the case of sample 3 very weak bands at 930 and 850 cm^{-1} are also observed. They are related with strongly degraded crystal lattice and may be easily interpreted as due to the AlAlOH and AlMgOH librations, respectively. The very weak band which appears at 3630 cm^{-1} corresponds to the stretching vibrations of OH groups. This observations confirm the supposition that the degradation of montmorillonite under the influence of HCl solution occurs through the removal of cations from octahedral layer. This results in the destruction of layer lattice and subsequent transformation of tetrahedral layer in amorphous silica.

The activation of montmorillonite by the HF solution (sample 2) gives at once the degradation and dissolution of the octahedral and tetrahedral

layers. X-ray diffractogram shows the decrease of intensity of montmorillonite reflections without broadening of them. It may be concluded that the undissolved part of the sample preserves a primary structure of montmorillonite. It may be interesting to mention that in the X-ray diffractogram the reflection of quartz (3.34 Å) appears. This reflection is not visible in the X-ray patterns of untreated sample and of the sample activated with HCl solution. This indicates that sample 2 is relatively enriched in this mineral. The IR spectrum (Fig. 2b) confirms the X-ray results. It reveals the absorption bands which are due to the presence of amorphous silica (the band 800 cm⁻¹, broadening of the bands in the range of 900—1300 and 420—500 cm⁻¹).

As seen from the Table 1 sample 2 contains a large amount of fluorine. It may be present partly in the crystal lattice of montmorillonite and partly as the component of secondary phases. The presence of fluorine in the crystal lattice of montmorillonite results from the possibility of substitution of both OH⁻ and O²⁻ ions by fluorine ions. In the case of O²⁻ ions the breaking of Si-O-Al bonds takes place. The presence of secondary phase Ca_{0.5}MgAlF₆ was shown by X-ray analysis. The IR spectrum of sample 2 shows a weak band at 590 cm⁻¹ which may be due to the vibrations of AlF₆³⁻ groups.

The activation of montmorillonite using KF solution (sample 5) results in the collapse of crystal lattice. The basal reflection shifts to about 12 Å. The large amount of fluorine allows to suppose that it is mainly combined in the secondary fluoride phases. The low content of amorphous silica (2.81%) and extraordinary low surface area indicate that the degree of degradation of montmorillonite is rather small. This conclusion is confirmed by the X-ray (Fig. 1e) and IR analysis (Fig. 2e).

Sample 4 is derivative of the sample 5. It is obtained by the two-stage activation: preliminary by KF solution and next by HCl solution. Sample 4 has similar properties to samples 2 and 3.

Sample 6 is obtained by the activation using the NH₄F solution and subsequent calcination. The X-ray (Fig. 1f) and IR (Fig. 2f) analysis indicate the preservation of montmorillonite structure. In this case the degree of degradation is very low. The amount of amorphous silica is distinctly small (3%). The change of the IR absorption spectrum in the range of 850—940 cm⁻¹ is possibly due to disordering of orientation of coordination polyhedra.

The catalytic activity and selectivity are expressed in terms of following formulas:

$$\text{activity} = \frac{\text{amount of converted cumene (moles)}}{\text{amount of used cumene (moles)}} \cdot 100$$

$$\text{selectivity} = \frac{\text{amount of product (moles)}}{\text{amount of converted cumene (moles)}} \cdot 100$$

Results of catalytic investigations are summarized in Table 2, in which the data are given obtained in successive 1, 5, 10 and 15th cumene pulses.

As can be seen, the major products are benzene and propylene. The small amount of ethylbenzene also appears. Some part of the products is deposited at the catalyst surface in the form of coke. The amount and strength of acid centres present on the catalyst surface is related to the

Table 2

Results of cumene cracking reaction

Sample	Activity %				Selectivity to benzene %				Selectivity to methylstyrene %			
	1*	5	10	15	1	5	10	15	1	5	10	15
1	98.6	87.4	73.5	66.7	19.9	9.17	2.18	1.25	0.0	1.98	8.1	10.6
2	100.0	99.1	92.6	87.4	24.6	19.3	24.0	24.1	0.0	0.03	1.59	2.19
3	95.3	94.8	92.0	82.1	61.3	72.9	87.2	89.1	0.4	0.5	0.9	1.33
4	95.3	93.7	94.0	84.1	56.0	60.2	37.6	44.3	0.4	1.02	1.85	4.6
5	62.1	54.3	49.5	25.7	5.5	4.8	3.14	3.0	3.62	9.64	19.2	35.8
6	99.5	99.2	99.1	98.3	55.7	67.4	56.6	62.2	0.0	0.0	0.0	0.0

* Amount of following cumene pulses.

catalytic activity in cumene cracking. Therefore, the catalytic activity can be taken as a measure of the acidity of the surface.

The dehydrogenation of cumene which results in α -methylstyrene as the product, is caused by the free radical processes. The selectivity to α -methylstyrene may be thus related to the amount of centres, which are able to generate the free radicals.

The samples of catalysts differed in the activity and selectivity as shown in Table 2. The natural, untreated montmorillonite (sample 1) has the high initial activity, which sharply decreases with the number of cumene pulses. Small amount of benzene and propylene is produced, but the amount of α -methylstyrene simultaneously increases. It can be easily interpreted as due to the formation of new radical centres, which are able to catalyze the dehydrogenation processes.

Samples 3 and 6 show high catalytic activity in the cracking of cumene. The high activity of sample 3 slightly decreases with the number of cumene pulses. The products are composed of high amount of benzene and propylene and small amount of α -methylstyrene.

Sample 6 has a high activity and selectivity to benzene and propylene. Moreover, the activity and selectivity are constant. No α -methylstyrene is formed on this catalyst.

Sample 5 has the worst catalytic properties. The activity is decreasing with the number of cumene pulses, small amount of benzene and large amount of α -methylstyrene being formed as products.

Samples 2 and 4 show intermediate properties. Their activity is relatively high but selectivity to products of cumene decomposition is rather poor.

The decrease of activity in the case of samples 1—5 may be related to the ability of the surface to α -methylstyrene polymerization.

CONCLUSIONS

The catalytic properties of montmorillonite are due to the presence of acid centres on the surface. The acid centres are generated by dissociation

of interlayer water and by the breaking of bonds in the sheets. In the case of cumene cracking the natural, untreated montmorillonite has a high initial activity which then decreases sharply. The activation which results in the increase of the amount of acid centres improves the catalytic properties of montmorillonite. Sample 6 shows the highest activity and stability. This sample is obtained by the heat treatment of montmorillonite activated with the NH_4F solution. Sample 3 which was obtained by activation in the HCl solution has a little smaller activity but the best selectivity.

The formation of the acid centres entails the destruction of structure, particularly octahedral layer. The joint activation by protons and F^- ions results in the best catalyst (sample 6). The influence of fluorine on catalytic properties of montmorillonite is not quite clear but it seems to play a very positive part as can be concluded by analogy with catalytic properties of alumina. The fluorination results in the increase of catalytic activity of alumina (Covini *et al.* 1967a, b).

The differences in selectivity are probably due to the difference in the type and strength of the active centres. In particular they may be related to the creation of new centres in the course of the catalytic reaction. Further studies are, however, required in order to determine their nature.

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Katarzyna BRÜCKMAN, Jerzy FIJAŁ, Jerzy HABER, Zenon KŁAPYTA, Tomasz WILTOWSKI, Witold ŻABIŃSKI

WPLYW RÓŻNYCH SPOSOBÓW AKTYWACJI NA WŁASNOŚCI KATALITYCZNE MONTMORILLONITU

Streszczenie

Przedmiotem badań były własności katalityczne naturalnego montmorillonitu i produktów jego aktywacji. Naturalny montmorillonit, wyseparowany na drodze sedymentacyjnej z bentonitu z Chmielnika, poddano aktywacji za pomocą roztworów HCl , HF , KF i NH_4F . Jedną z próbek następnie wyprażono. Przemiany strukturalne próbek badano metodą rentgenowską i spektroskopową w podczerwieni. Testowe badania własności katalitycznych w procesie krakingu kumenu wykonano metodą impulsową w temperaturze 350°C . Stwierdzono, że najwyższą aktywność katalityczną wykazują próbki aktywowane roztworem HCl oraz aktywowane roztworem NH_4F , a następnie prażone.

OBJAŚNIENIA FIGUR

Fig. 1. Dyfraktogramy rentgenowskie montmorillonitu z Chmielnika oraz produktów jego aktywacji

a — montmorillonit wyjściowy, b — produkt aktywacji roztworem HF , c — produkt aktywacji roztworem HCl , d — produkt aktywacji roztworem KF a następnie roztworem HCl , e — produkt aktywacji roztworem KF , f — produkt aktywacji roztworem NH_4F następnie wyprażony

Fig. 2. Widma absorpcyjne w podczerwieni montmorillonitu z Chmielnika oraz produktów jego aktywacji

a — montmorillonit wyjściowy, b — produkt aktywacji roztworem HF , c — produkt aktywacji roztworem HCl , d — produkt aktywacji roztworem KF a następnie roztworem HCl , e — produkt aktywacji roztworem KF , f — produkt aktywacji roztworem NH_4F następnie wyprażony

Катажина БРЮКМАН, Ежи ФИЯЛ, Ежи ХАБЕР, Зенон КЛАПЫТА, Томаш ВИЛЬТОВСКИ, Витольд ЖАБИŃСКИ

ВЛИЯНИЕ РАЗНЫХ СПОСОБОВ АКТИВАЦИИ НА КАТАЛИТИЧЕСКИЕ СВОЙСТВА МОНТМОРИЛЛОНИТА

Резюме

Объектом исследований были каталитические свойства природного монтмориллонита и продуктов его активации. Природный монтмориллонит, выделенный седиментационным путем из бентонита с Хмельника, был подвергнут активации растворами HCl , HF , KF и NH_4F . Затем один из

образцов был прокален. Структурные изменения изучались рентгеновским методом и инфракрасной спектроскопией. Тестовые исследования каталитических свойств в процессе крекинга кумена проведено импульсным методом в температуре 350°C. Установлено, что самую высокую каталитическую активность обнаруживают образцы активированные раствором HCl, а также активированные раствором NH₄Cl, а потом прокаленные.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Дифрактограммы монтмориллонита с Хмельника и продуктов его активации
a — исходный монтмориллонит, *b* — продукт активации раствором HF, *c* — продукт активации раствором HCl, *d* — продукт активации раствором KF, а потом раствором HCl, *e* — продукт активации раствором KF, *f* — продукт активации раствором NH₄F, потом прокаленный

Фиг. 2. ИК-спектры монтмориллонита с Хмельника и продуктов его активации
a — исходный монтмориллонит, *b* — продукт активации раствором HF, *c* — продукт активации раствором HCl, *d* — продукт активации раствором KF, а потом раствором HCl, *e* — продукт активации раствором KF, *f* — продукт активации раствором NH₄F, потом прокаленный