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Identification of super-active centers in thermally treated formamide-intercalated kaolinite

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Abstract

The thermal behavior of a formamide-intercalated mechanochemically activated (dry-ground) kaolinite was investigated by thermogravimetry-mass spectrometry (TG-MS) and diffuse reflectance Fourier transform infrared spectroscopy (DRIFT). After the removal of adsorbed and intercalated formamide, a third type of bonded reagent was identified in the 230 - 350 °C temperature range decomposing *in situ* to CO and NH₃. The presence of formamide decomposition products as well as CO₂ and various carbonates identified by DRIFT spectroscopy indicates the formation of super-active centers as a result of mechanochemical activation and heat treatment (thermal deintercalation).

The structural variance of surface species decreases with the increase of grinding time. The ungrounded mineral contains a low amount of weakly acidic and basic centers. After 3 hours of grinding, the number of acidic centers increases significantly, while on further grinding the super-active centers show increased basicity.

With the increase of grinding time and treatment temperature the amount of bicarbonate- and bidentate-type structures decreases in favor of the carboxylate- and monodentate.

Introduction

The use of carbon monoxide as a molecule for probing surfaces -such as aluminas and modified alumina surfaces- has been known for a considerable length of time.^{1,2} Such characterization determines the Brønsted and Lewis acid sites.² The advantage of using carbon monoxide or carbon dioxide as probe molecules rests with the fact that their infrared spectra lack the complexity of the spectra of molecules such as pyridine or sulfur dioxide. The molecules carbon monoxide and carbon dioxide probe base sites through chemical reactions with the base sites. Low temperature adsorption of carbon monoxide on aluminas acts as a selective probe of Lewis sites.³ Interestingly it was found that there was a linear relationship between the loss of intensity of the bands assigned to the hydroxyl groups and the increase in intensity of the absorbance of the CO species at 2200 cm⁻¹.¹ The effect of thermal treatment provided a mixture of Lewis acid sites on the alumina surface. The application of infrared spectroscopy as an effective tool for the determination of the probe molecule connecting to acid sites has proven most useful.¹⁻³ The thermal desorption of carbon monoxide has also been studied by infrared spectroscopy.⁴ Besides studies of the surfaces of various phase forms of alumina, characterization of the oxyhydroxides of aluminum including gibbsite and boehmite has also been carried out.^{2,3} The use of thermoanalytical methods including microcalorimetry offers a technique which provides complementary information to that of infrared spectroscopy.^{5,6}

Kaolinite is composed of a siloxane surface connected to a gibbsite-like one through an apical oxygen.⁷⁻⁹ This gibbsite like surface may be altered through chemical reactions with inserting molecules such as formamide, hydrazine and dimethyl sulfoxide.¹⁰⁻¹⁶ Thus it is possible that the kaolinite surface or a modified kaolinite surface may be likened to the active surfaces of the aluminas such as γ -alumina. One method of synthesizing surface active kaolinites is through mechanochemical activation.¹⁷⁻¹⁹ The mechanochemical modification of kaolinite through dry grinding results in a high surface area material with the potential for

having surface active sites on the mechanochemically activated surfaces.^{17,18} In this work we report the synthesis and characterization of a highly active surface through the thermal treatment of a formamide-intercalated mechanochemically activated kaolinite.

Experimental Section

The kaolinite mineral and intercalation. The kaolinite used in this study is from Szeg, Hungary. This mineral is a high defect kaolinite with a Hinckley index of 0.4. Intercalation was carried out by mixing 300 mg of the kaolinite with 5 cm³ of a 100 % formamide solution for 80 hours at room temperature. The excess solution was removed by centrifugation and the intercalated kaolinites were air-dried before thermoanalytical, XRD, and vibrational spectroscopic analyses.

Milling procedure. A Fritsch pulverisette 5/2-type laboratory planetary mill was used to grind the kaolin. Samples were ground for 0, 3 and 6 hours. Each milling was carried out with a 10 g air-dried sample in an 80 cm³ capacity stainless steel (18 % Cr +8 % Ni) pot using 8 (31.6 g) stainless steel balls (10 mm diameter). The applied rotation speed was 374 r.p.m.

X-ray powder diffraction. The XRD analyses were carried out on a Philips PW 3020 vertical goniometer equipped with curved graphite-diffracted beam monochromator. The radiation applied was CuK α from a long fine focus Cu tube, operating at 40 kV and 40 mA. The samples were measured in stepscan mode with steps of 0.02° 2 θ and a counting time of 1s. Data collection and evaluation were performed with PC-APD 3.6 software. Profile fitting was applied to extract information on the microstructure and structural defects of kaolinite and its alteration products.

Thermal analysis. Thermogravimetry/mass spectrometry (TG-MS) experiments were carried out in a Perkin-Elmer TGS-2 thermobalance coupled to a HIDEN HAL 2/301 PIC quadrupole mass spectrometer through a heated glass-lined metal capillary. Approximately 3 mg samples were heated in a platinum crucible at a rate of 10°C min⁻¹ in a flowing argon atmosphere of 99.995% purity. A portion of the evolved products was introduced into the mass spectrometer operating in the electron impact ionization mode at 70 eV. The intensity of 16 selected ions was monitored together with the thermogravimetric parameters. A linear interpolation was employed to correct the baseline shift of each ion curve. Intensities of m/z 16, 28 and 45 were corrected by taking into account the fragmentation of water and carbon dioxide. Thus, the ion m/z 45 corresponds to the molecular ions of formamide and the ions m/z 16, 18, 28 and 44 may represent fragment ions of formamide. The formation of these ions can be partially attributed to formamide fragmentation when they exhibit similar evolution profile as formamide molecular ion (at low temperature). However, at higher temperature the ions m/z 16, 18, 28 and 44 represents NH₂⁺ (from ammonia), water, carbon monoxide and carbon dioxide, respectively. It is noted that m/z 16 ion is plotted for ammonia rather than m/z 17 due to the disturbing effect of water fragment ion on the curve of the latter.

DRIFT spectroscopy. Diffuse Reflectance Fourier Transform Infrared spectroscopic (commonly known as DRIFT) analyses were undertaken using a Bio-Rad FTS 60A spectrometer. 512 scans were obtained at a resolution of 2 cm⁻¹ with a mirror velocity of 0.3 cm/sec. Spectra were co-added to improve the signal to noise ratio. Approximately 3 mg of ground kaolinite was dispersed in 100 mg oven dried spectroscopic grade KBr with a refractive index of 1.559 and a particle size of 5-20 μ m. Reflected radiation was collected at ~50% efficiency. Background KBr spectra were obtained and spectra ratioed to the background. The diffuse reflectance accessory used was designed exclusively for Bio-Rad

FT-IR spectrometers. It is of the so-called “praying monk” design, and is mounted on a kinematic baseplate. It includes two four-position sample slides and eight sample cups. The cup (3 mm deep, 6 mm in diameter) accommodates powdery samples mixed with KBr using an achate mortar and pestle in 1-3 % concentration. The reflectance spectra expressed as Kubelka-Munk unit versus wavenumber curves are very similar to absorbance spectra and can be evaluated accordingly. Spectral manipulation such as baseline adjustment, smoothing and normalization was performed using the Spectracalc software package GRAMS ® (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel ‘Peakfit’ software package, which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz-Gauss cross-product function with the minimum number of component bands used for the fitting process. The Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

Results and Discussion

Interpretation of the thermal decomposition processes of the organo-clay complexes is facilitated by the on-line MS and off-line DRIFT spectroscopic data. The TG and DTG curves show four different mass loss stages independently of the grinding time (Figs. 1-3). In the first step adsorbed formamide is liberated up to 130 °C with maximum rate at 90 - 100 °C, while the intercalated reagent is lost between 110 and 200 °C with DTG maxima in the 130 - 150 °C range. An unexpected decomposition process can be observed between 230 and 350 °C, while dehydroxylation of the thermally deintercalated mineral takes place in the 400 to 600 °C range. Mass spectroscopic ion intensity data show that in the 230 to 350 °C range the decomposition of strongly bonded formamide takes place resulting in the formation of H₂O, CO, CO₂, and NH₃. The continuous liberation of water is due to the formation of active centers to which mechanochemically dehydroxylated water is connected²⁰. It is interesting to observe, however, that the decomposition products (ammonia and carbon monoxide) of formamide strongly bonded to the surface show varying intensities as a function of the grinding time. It means that superactive centers of different acid-base properties are formed as a function of the grinding time having different affinities to decomposition products of different acid-base character.

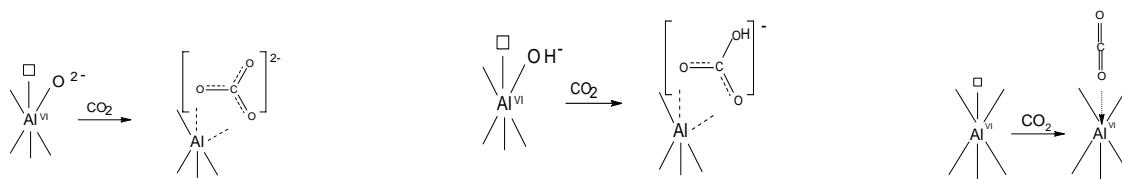
For a detailed investigation of this phenomenon intercalates of the clay ground for 0, 3 and 6 hours were heated to 200, 245, 290 and 345°C. After cooling the quenched samples to room temperature, the DRIFT spectra were recorded. The characteristic bands of carbon dioxide, carbonates and carbon monoxide appear in the 2400 - 1300 cm⁻¹ spectral range as shown in Figs. 4-6. The assigned bands are summarized in Table 1. Since intercalated formamide is lost up to 250°C, the amide bands are not observed in the spectra. In order to identify overtone and combination bands of the clay, samples of the kaolinite ground for 0 and 6 hours were heated to the same temperatures in a similar way and the spectra were recorded. Although combination and overtone bands do appear in the 2225 - 1630 and the 1900 - 1630 cm⁻¹ range showing decreasing intensity with the decrease of structural order (i.e. with the increase of the grinding time), they contribute little to the resolved bands.

Based on the TG-MS and DRIFT studies it can be stated that after the removal of formamide in two steps (adsorbed and intercalated) a third formamide mass loss stage can be found, leading to the *in situ* decomposition for ammonia and carbon monoxide. The decomposition products are bonded differently to the superactive surface in accordance with the acid-base properties developed during grinding. In the case of the ungrounded mineral most of the ammonia is liberated up to 200 °C, while CO and/or its derivatives are retained. With the increase of the grinding time, the relative retention of CO is decreased in favor of

ammonia (and carbon dioxide). Based on the MS and DRIFT data, the following questions need to be answered:

- (i). The presence of carbon dioxide and carbonates are confirmed by several bands in the 2400 - 1300 cm^{-1} spectral range. What is the origin of CO_2 in the system (see Table 1)?
- (ii). It is difficult to interpret the 1630 - 1600 cm^{-1} range in samples heated to 245°C and above. Are there bicarbonates or chemisorbed water formed by proton migration present? (MS results show the liberation of water with decreasing intensity prior to dehydroxylation).
- (iii). Is the formation of the superactive surface having selective sorption properties in the 200 - 350 °C range due to the temperature, the effect of grinding or to thermal deintercalation?

A possible explanation for the presence of CO_2 is the disproportionation of CO ($2 \text{CO} \rightarrow \text{CO}_2 + \text{C}$). For further possible explanations of the presence of carbon dioxide as well as the interpretation of the acid-base properties of the superactive centers formed, the extended literature of the surface characterization of $\gamma\text{-Al}_2\text{O}_3$ can be used. Carbon monoxide can form CO_2 in a catalytic process in which coordinately unsaturated (cus) cations play an important role^{2,5}. Carbon-dioxide formed can be connected to the surface in different carbonate forms, depending on the number of cus-cations:



The appearance of bands characteristic of end-on type CO_2 complexes as well as carbonates of varying structures can be verified by these processes.

Bands in the 1637 - 1607 cm^{-1} range are assigned as water β_{OH} bands. According to literature sources coordinately unsaturated sites of aluminum-octahedra can be occupied by water.^{2,4,5,21} These bonds are weaker than covalent bonds, but stronger than the coordinate ones. The fact that water is present even at 350°C can be explained by the presence of this type of coordinated water. This idea can be supported by the occurrence of a broad, associated water band in the OH stretching vibration region. In our judgement the presence of the band assigned to a β_{OH} vibration can also justify the supposition that a so-called proton migration takes place resulting in the formation of water coordinated to the aluminum-octahedra.²² Based on Figs. 4-6 the following conclusions can be drawn:

- (1) The structural variance of surface species decreases with the increase of grinding time (i.e. with the decrease of structural order).
- (2) The number of active sites capable of forming end-on type CO_2 complexes decreases with the increase of grinding time. The structure of the bonded species is definitely shifted to a carbonate-type structure.
- (3) In parallel with the occurrence of carbonate-type structures (i.e. with the increase of grinding time and the temperature) the bridge-type structures show a decreasing tendency.
- (4) With the increase of grinding time and treatment temperature the amount of bicarbonate- and bidentate-type structures decreases in favor of the monodentate- and carboxylate-type ones.

The reasons for the formation of surfaces with changing acid-base properties in the 230-350 °C range shall be discussed. According to literature sources the acid-base character of a surface depends on the joint effect of the oxide neighbors, the coordination of the OH-groups and the captions, the number of coordinately unsaturated sites, as well as on the surface charge of the OH-groups.^{1-6,21,23} In the case of clay minerals it means that the acid-base properties of the surface are strongly influenced by metal oxides present as impurities, the occurrence of tetrahedral Al-coordination in the form of defect sites, as well as by the coordinately unsaturated sites formed as a result of thermal decomposition processes.

The acid-base properties of the superactive surface can be characterized by the differences in adsorbing CO, NH₃ and CO₂. The νOH stretching range cannot be used as an information source due to the extreme complexity of the system. In the case of the ungrounded sample (Fig. 1) CO -and with a high baseline CO₂- can be detected in the evolved gases above 200 °C. Considering the weak basic character of CO and the medium acid-strength of CO₂, the surface contains a low amount of weakly acidic and basic centers. After 3 hours of grinding, the number of acidic centers increases significantly: the intensity of the weakly basic CO and that of ammonia as a base of intermediate strength increases. After 6 hours of grinding the basicity of the superactive sites increases (increased CO₂ retardation), though their number decreases.

These observations are in harmony with the statements of Morterra^{2,23} and Knötzing³ as well. Considering that in the 2000 - 1200 cm⁻¹ range of the DRIFT spectra the characteristic bands of carbonate-type structures connecting to basic centers appear with the increase of the grinding time, it is believed that the superactive sites formed in the 230-350 °C range can mainly be connected to the Al-octahedra of the kaolinite.

It can be assumed that the occurrence of superactive centers can primarily be due to the structural disorder obtained as a result of thermal deintercalation and grinding together. If either grinding or thermal deintercalation could form superactive centers alone, the sample would absorb CO₂ from the air, which is obviously not the case. The occurrence of the β_{OH} band in the 1637-1600 cm⁻¹ range at high temperature is rather interesting. This indicates the presence of coordinately very strongly bonded water in the system. The broad bands in the OH stretching range also supports this idea.

Conclusion

The use of thermogravimetry combined with mass spectroscopy is indispensable in an attempt made to reveal the mechanism of complicated decomposition processes accompanied with the simultaneous liberation of gaseous decomposition products. Interpretation of the thermolysis processes is much more reliable if the surface composition is also followed as a function of the temperature by means of a vibrational spectroscopic technique. The DRIFT technique is the method of choice in such investigations. This multi-method approach proves to be very efficient for the study of surface-modified kaolinites.

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Legends

Figure 1. TG-DTG and ion intensity curves of formamide-intercalated kaolinite ($m/z = 16$: NH_2^+ , $m/z = 18$: H_2O^+ , $m/z = 28$: CO^+ , $m/z = 44$: CO_2^+ , $m/z = 45$: $\text{CHO}(\text{NH}_2)^+$).

Figure 2. TG-DTG and ion intensity curves of kaolinite ground for 3 hours and intercalated with formamide ($m/z = 16$: NH_2^+ , $m/z = 18$: H_2O^+ , $m/z = 28$: CO^+ , $m/z = 44$: CO_2^+ , $m/z = 45$: $\text{CHO}(\text{NH}_2)^+$).

Figure 3. TG-DTG and ion intensity curves of kaolinite ground for 6 hours and intercalated with formamide ($m/z = 16$: NH_2^+ , $m/z = 18$: H_2O^+ , $m/z = 28$: CO^+ , $m/z = 44$: CO_2^+ , $m/z = 45$: $\text{CHO}(\text{NH}_2)^+$).

Figure 4. DRIFT spectra of formamide-intercalated kaolinite heated to different temperatures.

Figure 5. DRIFT spectra of kaolinite ground for 3 hours, intercalated with formamide and heated to different temperatures.

Figure 6. DRIFT spectra of kaolinite ground for 6 hours, intercalated with formamide and heated to different temperatures.

Table 1. Assignment of DRIFT bands and the schematics of the proposed surface structures

Spectral range (cm ⁻¹)		Structure ^{1-6, 21-23}
Measured data	Literature data ^{1-6, 21-23}	
(1)end-on complex 2345-2341	2360-2343	Al···O=C=O
(2)linear	2110-2065 2215-2203 (depending on strength of bonding)	Al-O···C≡O
(3)bridge 1817-1755 1853-1819	1860-1780 (ν _s) 1280-1250 (ν _{as}) 1000 (γ _{COO⁻})	
(4)bidentate 1698-1637	1670-1600 (ν _s) 1310-1280 (ν _{as}) 1050-980 (γ _{COO⁻}) 830	
(5)bicarbonate 1637-1607 1500-1400	3600 ν _{OH} 1630-1615 (ν _{as}) 1500-1400 (ν _s)	
(6)carboxylate 1581-1637 1393-1357	1630-1570 (ν _{as}) 1390-1350 (ν _s)	
(7)monodentate 1581-1451 1393-1313	1540-1420 (ν _s) 1390-1330 (ν _{as}) 1050-980 (γ _{CO})	
coordinatively bonded water 1637-1600	1640-1605 (β _{OH})	

Table 1. Horváth et al.