Research Article

Dimethyl Sulfoxide Species Entrapped by Raw and Acid-Activated Sepiolite Framework

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Abstract

Novel hybrid organic-clay materials were prepared by interaction of dimethyl sulfoxide molecules in the interlayer space of raw and acid activated sepiolite composites. The structural and thermal properties of the hybrid materials, raw and acid activated sepiolite were examined by using Fourier transform infrared, thermal analysis, X-ray powder diffraction and surface area measurement techniques. Thermal analysis data prove the remarkable effects of acid activation on the framework of sepiolite which are reflected by the intercalation mechanism proceeding through the replacement partly of the interstitial water by dimethyl sulfoxide species. The protons are directly involved in the actual structure and thus enhances the thermal stability of the complex between dimethyl sulfoxide and the sepiolite. The noticeable surface area increase of activated sepiolite than that of the raw one is connected to the micropore formation. The data presented in this study may also provide further insight into catalysis studies and the application of clays in the growing field of environmental management.

Keywords: dimethyl sulfoxide, sepiolite, interstitial water, thermal stability.

Ham- Asitle Aktive Edilmiş Sepiyolit Örgüsü Tarafından Alıkonulan Dimetil Sülfoksit Türleri

Öz

Dimetil sülfoksit moleküllerinin saf ve asit aktive sepiyolit killerinin içtabaka boşluğunda etkileşmesiyle yeni melez organik kil materyalleri hazırlandı. Saf sepiyolitin, asit aktive edilmiş sepiyolitin ve elde edilen hibrit malzemelerin yapısal ve termik özellikleri, Fourier dönüşümlü kızılötesi, termik analiz, X-ışını toz kırınımı ve yüzey alanı ölçüm teknikleri kullanılarak incelendi. Termik analiz verileri asit aktivasyonun sepiyolitin yapısına yaptığı olağanüstü etkileri ve dimetilsülfoksit türlerinin sepiyolitteki iç tabaka suyunun bir kısmı ile yer değiştirme mekanizmasıyla araya-sızdığını kanıtlamaktadır. Protonlar doğrudan mevcut yapı ile ilişkilidir ve dimetil sülfoksit-sepiyolit kompleksinin termik kararlılığını artırır. Saf sepiolite nispeten aktive edilmiş sepiyolitin yüzey alanındaki fark edilebilir artış mikrogözenek oluşumuyla ilişkilidir. Bu çalışmada sunulan veriler daha sonraki kataliz çalışmalarına ışık tutabilir ve gelişen çevre yönetimi alanında killerin kullanılmasına katlıda bulunabilir.

Anahtar kelimeler: dimetil sülfoksit, sepiyolit, doku suyu, termik kararlılık

Introduction

Clays are widely used as adsorbents, rheological control agents, ion exchangers of metal ions from aqueous medium in many fields of industry because they possess significant physical–chemical properties such as high surface areas, strong adsorption abilities, porosities, high cation exchange capacity, hydration and excellent swelling properties [1-6]. The structural properties of clays determine and limit their potential applications. Various processes such as acid activation, organoclay synthesis, intercalation, calcination and pillaring have been employed to modifying these structural properties of clays [7-11]. The potential of acting as a replacement intermediate of organoclay derivatives has been of interest by many researchers [12-15].The organoclay synthesis, utilized mostly for modifying the structural and surface properties of clay minerals, is an important process to obtain novel materials with desired properties [12-15]. Although extensive studies on surfactant intercalation into bentonite clays have been conducted, there seemed to be no reports on dimethyl sulfoxide (DMSO) modified sepiolite. The chemistry of DMSO-composites retained by modified sepiolites should represent a clear possibility of new and promising materials.

In present study, the structural features of DMSO-sepiolite and DMSO-acid-activated sepiolite composites were investigated by using Fourier transform infrared (FTIR), thermogravimetry-derivative thermogravimetry (TG-DTG) and differential thermal (DTA) analyses, X-ray powder diffraction (XRD) and surface area measurement techniques.

Experimental

A purified sepiolite originally from Eskisehir, Turkey and 1 N H_2SO_4 (1:1 mass ratio) were mechanically stirred under reflux for 4 h at 90 °C and the resulting solids were washed with twice distilled water repeatedly. The supernatant was centrifuged at 2000 rpm and the dried product was sieved to 212 μm finally. Approximately 2 g of the sepiolite sample was thoroughly refluxed with spectral grade DMSO for 3 days at 25 °C under N_2 atmosphere. Infrared spectra in the range of 4000-200 cm^{-1} were recorded at a resolution of 4 cm^{-1} on a Mattson-1000 FTIR instrument. Simultaneous TG, DTG and DTA analyses were carried out on a Rigaku TG 8110 thermal analyzer combined with TAS 100 (range 25-1000 °C) under nitrogen flow (40 ml min^{-1}) with a heating rate of 10 °C min^{-1}. XRD patterns were traced on a Rigaku 2200 automated powder diffractometer using Ni-filtered CuKα radiation (λ, 1.54050 Å). Surface areas were measured by nitrogen adsorption at 77 K using Quantachrome Monosorb Analyzer.

Results and Discussion

Shown in Fig. 1(a-b) are the comparative FTIR spectra of nonintercalated and intercalated sepiolite samples; the band of the triple bridge group Mg_3OH at 3697 cm^{-1}, the feature of the structural water at 3474 cm^{-1}, the stretches associated with inner-surface hydroxyls and interstitial water at 3619 and 3451 cm^{-1}, respectively and the OH-bending mode at 1660 cm^{-1}. The Si-O combination modes at 1213, 1090 and 987 cm^{-1}, the Si-O-Si basal plane vibrations at 1019 and 474 cm^{-1}, the peak at 442 cm^{-1} arising from the Si-O-Mg linkage and the Mg_3OH bending mode at 655 cm^{-1} are attributable to the lattice vibrations [16]. Dolomite impurities give rise to the 1440 cm^{-1} band. The IR patterns of Sep/DMSO derivative showed striking variations within the characteristic O-H axial deformation region. A careful examination of the spectra suggests that the 3474 and 3440 cm^{-1} bands are interrelated in that the recessed location of the inner hydroxyl groups account for the considerable intensity decrease of the 3619 cm^{-1} band in parallel with the extent of intercalation. The downward shift and the intensity decreases of the OH and bending stretches

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of interstitial water together with the symmetric C-H feature at 2915 cm^{-1} [Fig. 1(b)] could indicate the DMSO species embedded in the gallery space of sepiolite by substituting partly the interstitial water [17-18]. The 1660 cm^{-1} bending mode of water weakened and furthermore, the skeletal stretches between 1200 and 400 cm^{-1} disappeared due to permanent breakdown of the octahedral layer under the disruptive effect of acid [Fig. 1(c)]. The tetrahedral units of acid-treated sepiolite in particular, was markedly disturbed after treatment with DMSO which resulted in the frequency shifts of the Si-O stretches at 1213 and 1166 cm^{-1} and a very prominent band associated with the cointercalated DMSO and water units within the sepiolite matrix emerged at 3434 cm^{-1} [Fig. 1(c-d)] [18-19]. The low-frequency modes of the intercalated species which are suppressed by the intense bands related to the framework of sepiolite and the reduced intensity of the 940 cm^{-1} band in the spectrum of the Sep/DMSO composite complement the appearance of the stretches at 1155 and 1101 and support the hypothesis that, of different hydroxyls, the inner-surface hydroxyl groups contributed most to the hydrogen bonding directly with the DMSO intercalates [20]. Although a measurable amount of DMSO has been intercalated, the IR spectrum of the activated sepiolite derivative is not significantly different from that of nonintercalated sepiolite except some very weak bands (1511 and 1462 cm^{-1}) and a slightly weakened bending mode at 940 cm^{-1} [Fig. 1(d)]. Therefore, it seemed that the dolomite impurities that are distributed on the interior surfaces may have made interlayer diffusion more difficult and contributed to a weaker inorganic host-guest interaction.
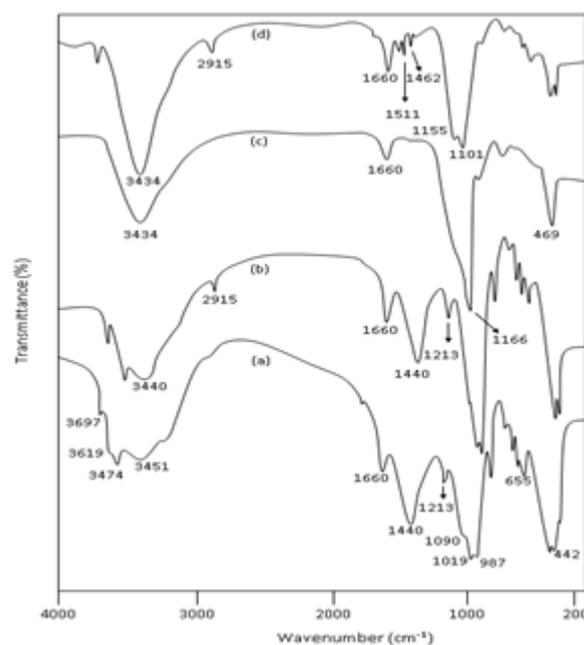

Fig. 1. FTIR spectra of (a) raw sepiolite, (b) Sep/DMSO composite, (c) activated Sep and (d) activated Sep/DMSO composite.

Two endothermic peaks at 25-105 and 180-252 ºC with the mass losses by 1.92 and 0.60 %, respectively, on the DTG curves of the raw sepiolite correspond to the desorption of humidity and "chemisorbed" water [Fig. 2(a)]. A small loss of mass (ca. 1.79 %) observed at 232-326 ºC represents the removal of bound water. The bigger mass losses (3.25 and 3.25 %) of the raw Sep/DMSO composite than that of the raw sample (1.92 and 0.60 %) in the temperature ranges 25-105 and 158-240 ºC implicate the fact that the DMSO molecules are immobilized through ion-dipole interactions with the mobile cations. In these interactions, the organic groups are grafted by covalent bonds to the silicate sheets, which permits obtaining more thermally and chemically stable entities [20, 21]. Furthermore, chemical displacement of bound water by DMSO generated a gradual mass loss up to 4.82 % at a higher temperature interval (290-453 ºC). After that, a wide range of overlapped dehydroxylation and decomposition processes occurred in the temperature ranges 580-720 and 725-823 ºC whereas the phase transition at 850 ºC [18] was the last exothermic event of the DTA profile [Fig. 2(b)]. The penetration ratio of DMSO

into the channels of raw sepiolite calculated from present thermoanalytical data is about 20 % [1]. The activated-Sep/DMSO illustrates two distinct endothermic peaks (mass losses by 1.55 % and 10.78 %, in the temperature ranges 71-113 and 118-345 ºC, respectively) which may be collectively ascribed as partial oxidation and then elimination of the interlamellar organic matter from the

sepiolite host [Fig. 2(c-d)]. The protons are not only required to provide access to interstitial water but also are directly involved in the actual chemistry and thus enhances the stability of the complex between DMSO and the sepiolite notably.
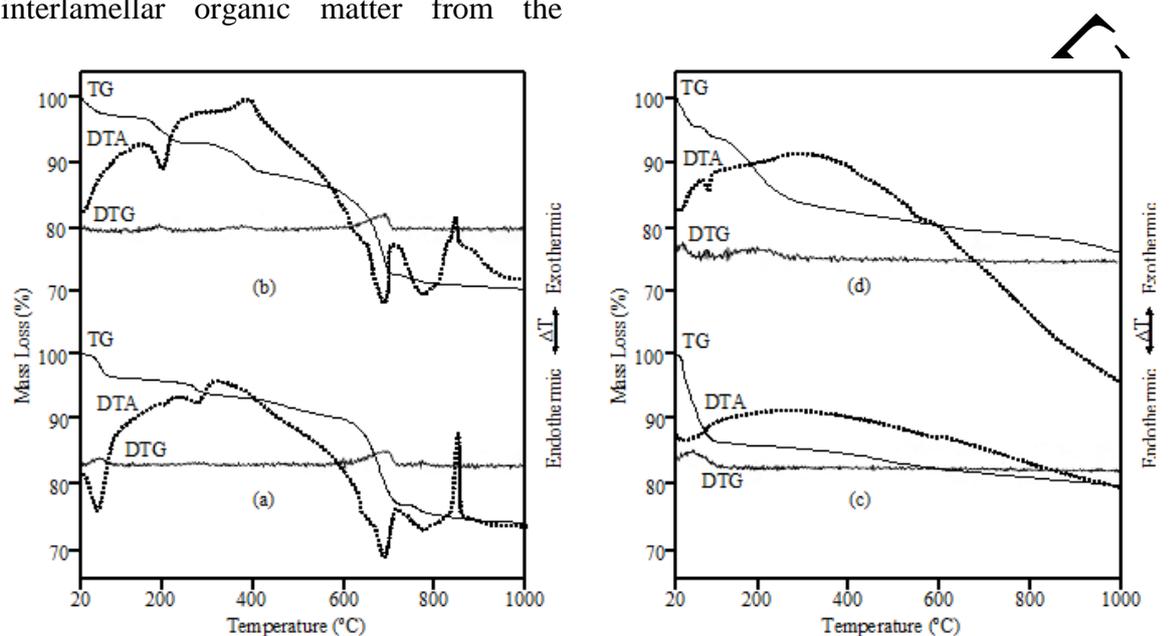

Fig. 2. *DTA/TG/DTG measurements of (a) raw sepiolite, (b) Sep/DMSO composite, (c) activated Sep and (d) activated Sep/DMSO composite.*

True intercalation of DMSO composites into sepiolite has been confirmed by strong XRD reflections [Fig. 3(a)] of 7.04° and 7.12° (2θ) at d(110) values 12.55 and 12.42 Å, respectively, and a peak reflection at 19.67° 2θ (130) and several very weak reflections [22]. The strong peaks at 30.88° and 41.04° 2θ in the XRD spectrum of raw sepiolite are due to the dolomite impurity. In relation to raw sepiolite, the intensity of the sepiolite basal lattice parameter of 7.04° (2θ) decreases because of the DMSO molecules intermolecularly bonded with interstitial water and a new d(110) peak of value 13.38 Å at 6.60° (2θ) arises from the

inclusion of DMSO into the channels [Fig. 3(b)]. The interlamellar expansion of 0.8321 Å that is much less than the dimensions of the DMSO molecule may be interpreted in terms of a keying incorporation of some of the DMSO species within the region. However, the structural geometry may also allow the DMSO to conform itself to give the least expansion consistent with minimum interaction between neighbouring molecules since the other peaks in raw-Sep/DMSO almost unchanged with respect to raw sepiolite [19, 20].
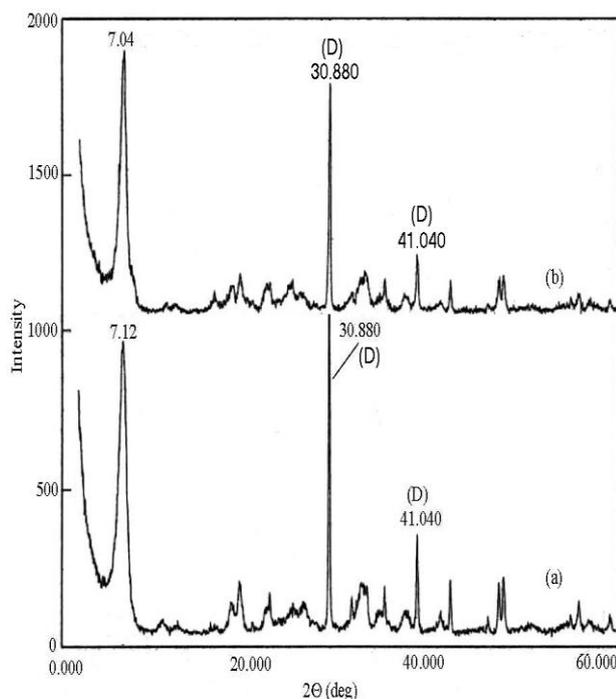
Fig. 3. *X-ray diffractograms of (a) raw sepiolite and (b) Sep/DMSO composite*

The surface area increase from 165 to 265 $m^2 g^{-1}$ on acid treatment may be connected to the increased number of micropores as a result of the structural irregularities of the host framework. It is not surprising that the conversion of the original micropores (≤ 2 nm) to mesopores (2-20 nm) by the retained DMSO species primarily favor the surface area decrease of both the activated and raw sepiolites from 265 to 177 $m^2 g^{-1}$ and from 165 to 80 $m^2 g^{-1}$, respectively [23,24]. Remarkable effects of acid activation on particle size and channel micropore lengths are reflected by a higher mass loss of activated sepiolite than the raw one. The data prove that the intercalation process proceeds through the chemisorption and then decomposition of the adjacent silicate layers' DMSO species which lead to irreversible changes in the sepiolite structure eventually.

Conclusions

The weakening of the stretching and deformation peaks of hydroxyls of sepiolite at 3774, 3619 and 1660 cm^{-1} reveal the presence of host–guest interactions between the sepiolite and DMSO species. Characteristic vibrational features of hybrid materials were supported by the thermal analysis data and the X-ray diffraction pattern. Thermal analysis data showed that the intercalated DMSO species were thermally more stable than raw DMSO molecules. The incorporation of some of the DMSO species into region of sepiolite caused a change of basal spacing values. The surface area of pure sepiolite is affected by the incorporation of DMSO molecules within the gallery spacing. The results obtained in this study may provide further insight into electrochemical and catalysis studies. Also DMSO-sepiolite materials may be utilized for developing new clay-based hybrid materials exhibiting comparatively higher thermal stability.

Acknowledgment

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