Modification and Characterization of Nanotubular Halloysite for Heterogeneous Catalytic Applications

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Introduction

Nanotubular Halloysite is of growing interest as a catalyst, catalyst support and template material because of its nanostructure, chemical characteristics and recent geologic deposit discoveries in New Zealand and Idaho and small business activities (NaturalNano). Halloysite has for a number of decades been considered for use in heterogeneous catalytic systems from cracking [1] to selective oxidation [2]. However, to date, there has not been a broad consideration of Halloysite from a combined clay chemical and heterogeneous catalytic perspective. Given the multiple chemical and physical steps in catalyst chemistry from creation to regeneration, it is important to examine the solution, dispersion, thermal and surface properties of Halloysite.

Two principal modifications of Haloysite exist: a hydrous form with the composition $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$ and a form with a composition and structure near to that of kaolinite, $Al_2Si_2O_5(OH)_4$. The latter form has a *c*-dimension of about 0.72 nanometers. The hydrous form has a *c*-dimension of about 1.01 nm. Drying converts the hydrated form to a less hydrous one spontaneously and irreversibly. Halloysite has a larger cation exchange capacity, surface area, and catalytic activity than does kaolinite.

The opportunity for discovery of new catalytic systems with Halloysite is large. The deposit of Halloysite in Idaho is particularly abundant and low in iron which in the past has limited the usefulness as catalysts. The nanotubes of these materials are several microns long and have a diameter of 100 to 200 nanometers. The unique feature of the nanotubes is that there is a lumen that runs the length of the tube that is 30 nanometers in diameter. This channel is studded with reactive hydroxyls that can undergo condensation reactions with silane coupling agents. This will allow a whole variety of functionalities to be placed in the channel including ion exchange capacity. This approach will also allow the nanochannel to be filled with catalytic sites that will create nano-confined reactors.

Materials and Methods

Hollysite from the Idaho (NaturalNano) has been examined by analytical scanning electron microscopy (ASEM) using a Hitachi 3400, by analytical centrifugation (AC) using a LumiSizer, by X-ray diffraction (XRD) using a Bruker D8 GADDS (general area detector diffraction system), by Fourier Transform Infrared Spectroscopy (FTIR) using a Bruker Tensor 27, by thermal analysis using a Netzsch STA 449C Jupiter, TG/DSC and by temperature programmed methods using a Hiden CatLab. Solution dispersion stabilities and particle sizes were determined from varying pH and solution additives for viscosity control for various Halloysite samples. XRD has been used to examine the structure of normal, collapsed and expanded halloysite (expanded with water, formamide or dimethyl sulfoxide) via its basal peak [3]. FTIR has been used to track the changes in structural vibrations and the various OH vibrations. Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTGA) have been used to examine the dehydroxylation and other thermally caused changes of halloysite. Temperature programmed desorption (TPD) of various probe molecules (H_2, CO, and NH_3) has been used to examine the surface chemistry of various natural and modified Halloysite samples.

Results and Discussion

Results for the AC and the TPD provided valuable surface chemistry and will be detailed, in the presentation. The ASEM (Fig 1) provided visual and elemental changes in variously treated Halloysites relatable to catalyst life cycles.

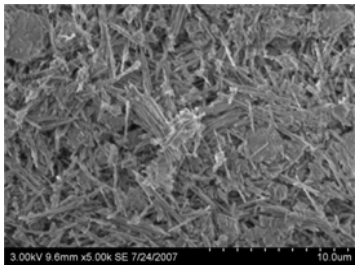

Figure 1 Halloysite-SEM micrograph

FTIR provided the infrared stretching frequencies of the inner-surface hydroxyls (3695, 3670, and 3650 cm^{-1}) and the inner hydroxyls absorbing at 3620 cm^{-1} [3]. The FTIR spectra show identifying bands of both OH and Si-O-stretching bands and Al-O-Si-bending vibrations. Halloysite is characterized by the 459 cm^{-1} band due to the Si-O bending vibration [4, 5].

XRD and TA proved invaluable to trace the structural changes induced by the chemical and thermal treatments. TA showed hydrated Halloysite exhibits an endothermic peak at ~50ºC due to hydroscopic and interlayer water with additional water being lost at ~ 430ºC [3].

Results and conclusions will be discussed in terms of the life cycles of various catalytic systems with emphasis on impregnation, calcinations and regeneration in correlation to other projects [6].

References

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