MICROSTRUCTURE OF HDTMA\textsuperscript{+}-MODIFIED MONTMORILLONITE AND ITS INFLUENCE ON SORPTION CHARACTERISTICS

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Abstract—A series of organoclays with monolayers, bilayers, pseudotrilayers, paraffin monolayers and paraffin bilayers were prepared from montmorillonite by ion exchange with hexadecyltrimethylammonium bromide (HDTMAB). The HDTMAB concentrations used for preparing the organoclays were 0.5, 0.7, 1.0, 1.5, 2.0 and 2.5 times the montmorillonite cation exchange capacity (CEC). The microstructural parameters, including the BET-N\textsubscript{2} surface area, pore volume, pore size, and surfactant loading and distribution, were determined by X-ray diffraction, N\textsubscript{2} adsorption-desorption and high-resolution thermogravimetric analysis (HRTG). The BET-N\textsubscript{2} surface area decreased from 55 to 1 m\textsuperscript{2}/g and the pore volume decreased from 0.11 to 0.01 cm\textsuperscript{3}/g as surfactant loading was increased from Na-Mt to 2.5CEC-Mt. The average pore diameter increased from 6.8 to 16.3 nm as surfactant loading was increased. After modifying montmorillonite with HDTMAB, two basic organoclay models were proposed on the basis of HRTG results: (1) the surfactant mainly occupied the clay interlayer space (0.5CEC-Mt, 0.7CEC-Mt, 1.0CEC-Mt); and (2) both the clay interlayer space and external surface (1.5CEC-Mt, 2.0CEC-Mt, 2.5CEC-Mt) were modified by surfactant. In model 1, the sorption mechanism of p-nitrophenol to the organoclay at a relatively low concentration involved both surface adsorption and partitioning, whereas, in model 2 it mainly involved only partitioning. This study demonstrates that the distribution of adsorbed surfactant and the arrangement of adsorbed HDTMA\textsuperscript{+} within the clay interlayer space control the efficiency and mechanism of sorption by the organoclay rather than BET-N\textsubscript{2} surface area, pore volume, and pore diameter.

Key Words—BET-N\textsubscript{2} Surface Area, HDTMA\textsuperscript{+}, Organoclay, Pore Size, Pore Volume, Sorption Efficiency, Surfactant Loading, Sorption Mechanism.

INTRODUCTION

Organoclays represent a family of materials with hydrophobic surfaces and are synthesized by modifying swelling clays with various surfactants. Over the last 50 years, organoclays have attracted great interest because of their potential use in a number of applications, such as sorbents for organic pollutants (Stackmeyer, 1991; Zhu and Chen, 2000; Zhu et al., 2000), clay-based nanocomposites (Ray and Okamoto, 2003), and precursors for preparing mesoporous materials (Ishii et al., 2005).

It is well known that montmorillonite is hydrophilic in nature due to the cations within its interlayer region, making natural clays ineffective sorbents for organic compounds. Modifying clay mineral surfaces with surfactants to convert the hydrophilic silicate surface to an organophilic surface is a strategic step in the preparation of clay-based sorbents for organic pollutants (Bergaya and Lagaly, 2001). Various organoclays have been synthesized using different surfactants, including single and dual cationic surfactants (Smith and Galan, 1995; Zhu et al., 1998; Wang et al., 2004; Yilmaz and Yapar, 2004), anionic-cationic surfactants (Regev and Khan, 1996; Zhu and Chen, 2000) and non-ionic surfactants (Shen, 2001). The sorption capacity of organoclays increases with the surfactant loadings within the clay interlayer space (Wang et al., 2004). Organoclays have been demonstrated to be effective as sorbents for organic pollutants in water (Smith and Galan, 1995; Zhu et al., 1998; Shen, 2001; Wang et al., 2004; Yilmaz and Yapar, 2004). Different sorption mechanisms are involved, depending strongly on the characteristics of the surfactants and organic pollutants used. For example, Boyd et al. (1988a) and Jaynes and Boyd (1991) showed that sorption of non-ionic organic compounds (NOCs) by large-alkyl organobentonites was essentially due to linear solute partitioning into the microscopic organic phase formed by the large alkyl chains of quaternary ammonium cations. Non-linear isotherms indicative of adsorption or co-sorption were observed when small-alkyl organobentonites were used as sorbents (Lee et al., 1990). Smith and Galan (1995) examined the properties of hybrid organobentonites...