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Improvement of physical characteristics of petroleum waxes by using nano-structured materials

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ABSTRACT

Layered double hydroxides (LDHs) are a class of synthetic two-dimensional nano-structured anionic clays whose structure can be described as nano-layered ordered material. This study aims to use nano-layered materials as a host for organic guests having required functional groups such as azo-compounds to alter LDH surface properties from hydrophilic to hydrophobic and increase sorption capacity for sulfur and aromatic compounds through constructing nano-hybrid material. A large anionic pigment (phenyl azobenzoic sodium salt) has been intercalated into Zn–Al LDH and a complex system of supra-molecular host–guest interactions was formed.

We have examined the unusual bi-functionality effects caused by hybridization for removing sulfur and aromatic compounds from petroleum waxes. Results clearly indicated that nano-layered material decreased sulfur content and mono-aromatic compounds of heavy slack wax. In the same run, it completely removed di-aromatic compounds. In the same trend, the nano-hybrid material showed high efficiency for removing aromatic and sulfur compounds from crude petrolatum. This leads to an improvement for the physical properties of heavy slack wax and crude petrolatum.

1. Introduction

Petroleum waxes are broadly defined as the waxes naturally present in various fractions of crude petroleum. Originally, they were considered as by products in the dewaxing of lubricating and gas oils, but, today they are valuable products for many industrial applications [1]. Petrolatum is obtained from certain types of heavy petroleum distillates or residues. It is a base material for manufacturing of medicinal petroleum jelly [2].

In this century, petroleum waxes have been widely used in many applications such as candles, polishes, treatment of paper and cardboard, printing inks, production of laminated foils and papers for the food industry, cosmetics and pharmaceutical industries, and other industrial purposes [3].

Layered double-metal hydroxides (LDHs) are nano ordered layered inorganic compound having ability to intercalate anionic compounds, because LDHs are constituted by infinite sheets of brucite-type material charged positively, where divalent cations are replaced in a fraction of x by trivalent cations in octahedral coordination. The general formula for these compounds is $(M2_{1-x}M3_x(OH)_2)^{x+} \cdot (A^-)_x \cdot nH_2O$, where M2 and M3 are divalent and trivalent cations, respectively and "A" represents interlayer anion that leads to the electrical neutrality of the compound. The distance between two adjacent layers depends mainly on the nature of the interlayer species and their electrostatic interaction with the main layers. These nano-layered materials can be used as hosts for organic guests having required functional groups to alter LDH surface properties from hydrophilic to hydrophobic and increase sorption capacity for non-ionic organic compounds.

Recently, various hetero-structured hybrids such as inorganic/inorganic [4], organic/inorganic [5], and bio/inorganic [6] systems have attracted considerable research interests due to their unusual physicochemical properties.

A few reports [7–9] have been published on the use of organic-modified LDH for removing organic pollutants and results indicate the further potential of these materials for that purpose. For example, Dutta and Robins [10] found that sorption of large guest molecules, e.g., pyrene, by an organic acid exchanged Li/Al-LDH could be regulated by varying the chain length of the carboxylic acids or type of anion with LDH. This sieving effect has been demonstrated in its application as a stationary phase in gas chromatography [9,11]. Despite numerous investigations of the intercalation reactions of organic anionic species in LDHs [12,13], detailed understanding of the resulting adsorptive properties for hydrocarbons is still lacking. Also, the ease of synthesis and structural controllability would make such LDH-based materials advantageous for practical applications, including in situ formation.

In this research, nano-layered material containing Zinc and aluminum was prepared and successfully used as a host for Azo dye

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to form nano-hybrid material. The nano-layered, and nano-hybrid materials were characterized by powder X-ray diffraction and scanning electron microscopy. The thermal properties of these prepared materials were also investigated by TGA and DTA. Furthermore, we have examined the unusual bi-functionality effects caused by hybridization for removing sulfur and aromatic compounds from petroleum wax.

2. Experimental

2.1. Materials

Two appropriate crude waxes; heavy slack wax and crude petrolatum obtained from two Egyptian companies; El-Ameria Refining Company and Alexandria Petroleum Company, respectively. The characteristics of heavy slack wax and crude petrolatum are shown in Table 1.

2.2. Preparation of nano-layered material

The Zn–Al LDH was prepared by co-precipitation of zinc and aluminum salts from homogeneous solution. A solution of zinc nitrate (5.94×10^{-2} mol) and aluminum nitrate (9×10^{-3} mol) were mixed with urea solution under vigorous stirring and heating [6,14–18]. The temperature of mixture was adjusted at 40–90 °C for long time. After filtration and washing several times in distilled water, the products were dried at 100 °C for 12 h.

2.3. Preparation of nano-hybrid material

Appropriate amount of azobenzene carboxylic acid sodium salt dissolves in 10 ml of deionized distilled water to make a concentration of 0.2 M with ultrasonic treatment. The LDH (0.24 g) was mixed with solution of sodium salts of organic acid under argon atmosphere and stirred at high temperature for 6 h. After filtration and washing, the samples were dried under vacuum at room temperature.

2.4. Adsorption treatment of the crude waxes

The adsorption technique was used to remove the undesired contaminated constituents (sulfur and aromatic components) from the crude waxes. This process was carried out via contacting technique using nano-layered material (as adsorbent) for heavy slack wax and nano-hybrid material (as adsorbent) for crude petrolatum. The nano-structured materials adsorbents were firstly activated at 120 °C for 2 h. For contacting technique, the wax was firstly heated to temperature of 90 °C, and then small amount of adsorbent was added gradually from time to time (until reached to 10 wt.% based on wax) with vigorous stirring for 1 h. The nano-structured materials separation was carried out via centrifugation [19].

Table 1
The physical characteristics and molecular type composition of heavy slack and crude petrolatum before and after adsorption processes.

Characteristics	Heavy slack	Heavy slack after adsorption	Crude petrolatum	Crude petrolatum after adsorption
Yield, wt.%	100	73.6	100	63.67
Congealing point, °C	62.5	63.5	70	72
Refractive Index, 210 °F	1.4402	1.4348	1.4561	1.4494
Sulfur Content, wt.%	0.28	0.19	1.29	0.520
Color (ASTM D-1500)	3.0	1.0	8.5	5.0
Molecular Type Composition				
Total Saturates	86.18	90	65.15	80
Total Aromatics	13.82	10	34.85	20
Mono-Aromatics, wt.%	11.52	10	21.90	20
Di-Aromatics, wt.%	2.30	–	12.95	–

2.5. Methods of analysis

The two crude waxes and the finished waxes were physically characterized according to American Society for Testing and Materials (ASTM) standard methods [20]. The standard methods for analysis are congealing point (ASTM D-938), refractive index (ASTM D-1747), and sulfur content by using X-ray fluorescence sulfur meter (ASTM D-4294).

The aromatic content of the crude waxes and the finished waxes was determined using liquid–solid column chromatography technique. A 1.3 cm diameter and height of 130 cm column packed with activated (60–200 mesh) silica gel was used [21]. The column was then moistened with 100 ml of *n*-hexane to dissipate the heat of adsorption. A 10-g sample of the soft wax dissolved in few milliliters of *n*-hexane was transferred to the column. The column was then eluted with 300 ml of *n*-hexane followed by 200 ml benzene and finally 100 ml of a 1:1 mixture of absolute methanol and benzene. Fractions of 25 ml were taken from the column, the solvent distilled off and the refractive index of each fraction was determined. According to the refractive index data at 20 °C, eluates were used into saturates, mono-, di- and poly-aromatics. The saturate hydrocarbons have refractive indices not more than 1.48. The mono-cyclic, bi-cyclic and poly-cyclic aromatics have refractive indices from 1.48 to 1.53, 1.53 to 1.59 and higher than 1.59, respectively [22].

3. Characterization

Powder X-ray diffraction (XRD) spectra were recorded on Rigaku, RINT 2200 using CuKα (filtered) radiation (λ = 0.154 nm) at 40 kV and 20 mA between 1.8° and 70°. Thermal analyses (TG, DTG and DTA) of powdered samples up to 800 °C were carried out at a heating rate of 10 °C/min in flow of nitrogen or air using a Seiko SSC 5200 apparatus. Scanning electron microscopy (SEM) was performed with JEOL: JSM-6330F (15 kV/12 mA).

4. Results and discussions

4.1. Powder X-ray diffraction

Nano-layered structure of Zn–Al LDH is used to be a host for azobenzene carboxylate anions which consider as a guest. The X-ray powder diffraction of Zn–Al–CO_3 LDH (Fig. 1) shows the basal peaks of planes *hkl* (003), (006), and (009). The good agreement between the values corresponding to successive diffractions by basal planes, i.e., $d(003) = 2d(006) = 3d(009)$ for Zn–Al LDH, reveals highly packed stacks of brucite-like layers ordered along axis *c*. Dimension *c* is calculated as three times the spacing for planes (003), i.e., 2.31 nm. The *c* dimension is equal to that reported for natural and synthetic hydrotalcite, 2.31 nm [23]. The XRD pattern of Zn–Al–CO_3 LDH has a main peak at 0.77 nm, which corresponds to interlayer spacing of the LDH in case of carbonate anions as a guest. This value is related to the thickness of the brucite-like layers (0.48 nm for hydrotalcite), as well as the size of carbonate anion (and, in some cases, its orientation) and the number of water molecules existing in the interlayer. The peaks of layered structure disappeared by the calcinations at 500 °C, and appearance of new peaks at high 2θ values as shown in Fig. 1b indicates the formation of metal oxides.

The reaction between host; Zn–Al LDH and guest; azobenzene carboxylate provided orange solids through host–guest interactions. The XRD pattern of this product is shown in Fig. 1c. New and strong reflections are observed at 2.8 and 1.9 nm and a weak reflection at 2.2 nm as shown in Fig. 1c with noticing that the original basal spacing of Zn–Al LDH disappeared. This means that the intercalation of