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Characterization and application of nano-alumina sorbents for desulfurization and dearomatization of Suez crude petrolatum

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ABSTRACT

High surface area γ-alumina adsorbents (302–376 m^2/g) were prepared by using different cationic surfactants in the presence of microwave irradiation. The adsorbents were characterized by DSC/TG, X-ray diffraction, nitrogen physisorption, and HRTEM techniques. To evaluate the influence of the surface features of alumina on its activity, its adsorption capacity for aromatic and sulfur compounds from petroleum waxes, Suez crude petrolatum was used for this investigation. Results clearly indicated that nano-alumina materials showed high efficiency for removing aromatics and sulfur compounds from Suez crude petrolatum. In the same run, it completely removed di-aromatics especially for AN5 sample. This leads to an improvement for the physical properties of Suez crude petrolatum which has been widely used in many applications such as household chemicals as candles and polishes, pharmaceutical, cosmetic as lipsticks, building construction, paper, match, rubber and other industrial purposes.

1. Introduction

γ-Alumina is one of the most important oxides used in the industrial applications. It is widely used as an adsorbent, catalyst, catalyst support, composite materials design and functional ceramics [1,2]. The textural porosity of the conventional γ-Al_2O_3 featured by a low surface area (less than 250 m^2/g), which limits its applications. Hence, over the past decade, the preparation of mesoporous γ-Al_2O_3 has received enormous research interests [3].

Many synthetic strategies have been developed based on surfactant assisted (template) sol–gel methods and organic additives [4,5]. Among these surfactant materials, cationic surfactants have been widely used for the synthesis of mesoporous aluminas [6]. However, these methods usually use the expensive and toxic aluminum alkoxides as precursors, and/or strictly control the synthetic conditions, which make them not convenient for the industrial scaling-up [7].

The commercial petroleum waxes may be divided into three principal groups: paraffin waxes, microcrystalline waxes and petrolatums. Petrolatum is a wax by-product obtained from certain types of heavy petroleum distillates or residues. It is a crude microcrystalline wax containing some oil. It is semi-solid, jelly-like materials. It is a base material for the manufacturing of medicinal petroleum jelly [8,9].

The most predominant deoiling process is the wax re-crystallization (fractional crystallization) which is sometimes called wax fractionation process and can be used to fractionate or deoil all types of waxes [9,10]. In our previous studies, we have used traditional deoiling techniques to produce different grades of petroleum waxes using different solvents at different temperatures [11–13].

Adsorption process used to remove polar compounds from petroleum waxes thus improving color, chemical, thermal and stability. O. Saber et al. used nano-layered, and nano-hybrid materials as an adsorbents for removing sulfur and aromatic compounds from petroleum waxes [14].

Thus, the present study is an attempt to prepare high surface area γ-alumina nano-adsorbents using different cationic surfactants in the presence of microwave irradiation. Also, the investigation of the activity and the adsorption capacity of the surface features of the prepared alumina for removing of aromatics and sulfur compounds from Suez crude petrolatum. Furthermore, this process can be a useful and an efficient method for the refining of Suez crude petrolatum since, it saves time, money and not causes damage to the environment because it done in one step using only 10 wt.% of prepared nano-materials while, the traditional methods, deoiling techniques, are done by two processes; fractional crystallization followed by adsorption techniques using expensive materials.

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2. Materials and methods

2.1. Materials

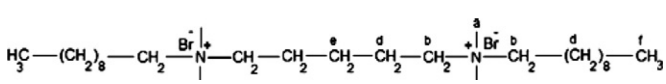
Aluminum nitrate nonahydrate (≥98%), ammonium hydroxide solution (28.0–30.0% NH_3 basis), glacial acetic acid (≥99.7%), decyltrimethylammonium bromide (DTAB, ≥98.0%), hexadecyltrimethylammonium bromide (CTAB, ≥98%), n-decyl bromide (98%), 1,5-dibromopentane (97%), diethyl ether (≥99.0%, anhydrous) and ethanol (≥99.5%, absolute) were all purchased from Sigma-Aldrich Company. N,N,N′,N′-tetramethylethylenediamine, (≤99%) was purchased from Merck Company. All reagents were used without further purification.

One appropriate crude petrolatum (petroleum wax by product) obtained from heavy residue from Suez Refining Company, Egypt used in this study for studying the effect of high surface area γ-alumina nano-adsorbents on removing both aromatics and sulfur compounds for improving the physical characteristics of Suez crude petrolatum.

2.2. Preparation of Gemini surfactants

2.2.1. N-Decanediyl-1,2-ethane bis (dimethylammonium bromide) surfactant

Stoichiometric molar ratios of N,N,N′,N′-tetramethylethylene diamine and decyl bromide were mixed with absolute ethanol, in a three-neck round-bottom flask fitted with a thermometer and condenser. The mixture was refluxed for 24 h. Ethanol was removed via rotary evaporator where a waxy product was obtained. The resulted product was extracted, using diethyl ether and re-crystallized from acetone/ethyl acetate mixture. The surfactant coded GS10-2-10.

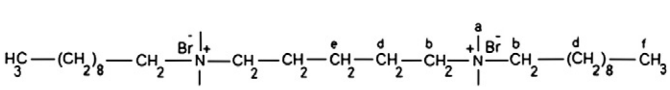


The structure of the produced Gemini surfactants was checked by elemental analysis, ^{1}H-NMR (Jeol-EX-270 MHz NMR Spectrophotometer), and mass spectroscopy (GC Mass-Qt 1000 EX Shimadzu, Japan E.I. 70 EV).

^{1}H NMR (MHz, δ, $CDCl_3$/TMS): (a) t, 3.83 ppm; (b) s, 3.44 ppm; (d) t, 3.17 ppm; (e) m, 1.67 ppm; and (f) t, 0.95 ppm (Fig. 1a). Mass spectrum: m/z = 554; $[M+1–^{81}Br]^+ = 474$; $[M–2Br/2]^+ = 199$. Anal. calc. for $C_{26}H_{58}N_2Br_2$: C, 56.32; H, 10.47; N, 5.05. Found: C, 56.43; H, 10.35; N, 5.24.

2.2.2. N-Decanediyl-1,5-pentane bis(dimethylammonium bromide) surfactant

Stoichiometric molar ratios of decyl-N,N-dimethyl amine and 1,5-dibromopentane were mixed with absolute ethanol, in a three-neck round-bottom flask fitted with a thermometer and condenser. The synthesis process was carried out in the same manner as described in the previous section. The surfactant coded GS10-5-10.



^{1}H NMR (MHz, δ, $CDCl_3$/TMS): (a) s, 3.52 ppm; (b) t, 3.30 ppm; (d) m, 1.65 ppm; (e) m, 3.14 ppm; and (f) t, 0.93 ppm (Fig. 1b). Mass spectrum: m/z = 600; $[M+1–^{81}Br]^+ = 520$; $[M–Br]^+ = 440$; $[M/2–C_5H_{10}] = 185$. Anal. calc. for $C_{29}H_{64}N_2Br_2$: C, 58.00; H, 10.67; N, 4.67. Found: C, 57.89; H, 10.83; N, 4.48.

2.3. Preparation of alumina

Five different γ-alumina powders were prepared using different surfactants as templates via microwave synthesis process. For all of the prepared samples, equal mole amounts of aluminum salt and surfactant (0.008 mol) were dissolved in deionized water, the pH value of the preparation medium was <3.

The mixture was titrated by ammonium hydroxide solution with continuous stirring; the addition process was stopped when the sol was formed at pH to ~8. The stirring continued for 8 min under the microwave irradiation at a power of 300 W. The product was centrifuged and washed by mixture of water and ethanol. The produced paste was dried at 90 °C overnight. The dried powders were calcined in a purified air at 400 °C with heating rate 5 °C/min for 6 h to obtain γ-Al_2O_3. All samples were sieved in the range of 70–90 μm.

Alumina samples based on aluminum nitrate precursor were prepared using commercial surfactants DTAB and CTAB and laboratory synthesized surfactants GS10-2-10 and GS10-5-10. The γ-alumina samples were coded as AND, ANC, AN2 and AN5 respectively.

According to the surface features of previously mentioned alumina samples (Table 1), an additional alumina sample was prepared based on a peptized synthesized aluminum hydroxide (0.008 mol) by glacial acetic acid (till pH ~1.8), using commercial surfactant CTAB. The resulted γ-alumina sample was coded AOC.

2.4. Characterization of solid samples

Differential thermal analyses coupled with thermogravimetric analysis (TGA) of the as-synthesized solid were recorded on a SDT Q600 Simultaneous DSC/TGA Analyzer manufactured by TA Instruments, Inc. (USA). The run was carried out in air at a heating rate of 10 °C/min. The crystalline structure of the prepared powders was analyzed by X-ray diffractometry (X-Pert PRO, PAN analytical, Netherlands) using CuKα radiation in the angular region of 2θ = 4°–70°. For phase identification purposes, automatic JCPDS library search and match were used. The surface area of different samples were determined from the adsorption of nitrogen gas at liquid nitrogen temperature (−195.8 °C) using NONA3200e (Quantachrome-USA). Prior to such measurements, all samples were perfectly degassed at 150 °C and 10^{-4} Torr overnight. High resolution transmission electron microscopy images (HRTEM) and scanning mode of TEM (STEM) were recorded on a JEOL JEM-2100 electron microscope at 200 kV.

2.5. Adsorption treatment of Suez crude petrolatum

The adsorption process was used to remove the undesired contaminated constituents (sulfur and aromatic components) from Suez crude petrolatum. This process was carried out via contacting technique using high surface area γ-alumina as an adsorbent. The nano-alumina sorbents 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-alumina sorbent separation was carried out via centrifugation [15].

2.6. Method of analysis

Suez crude petrolatum and the treated waxes were physically characterized according to American Society for Testing and Materials (ASTM) standard methods [16]. The standard methods for analysis are congealing point (ASTM D-938), refractive index (ASTM D-1747), oil content (ASTM D-721), color (ASTM D-1500) and sulfur content by using X-ray fluorescence sulfur meter (ASTM D-4294).