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Magnetic soot: Surface properties and application to remove oil contamination from water



Meruyert Nazhipkyzy^{a,b}, Araylim Nurgain^{a,b}, Marc Florent^c, Alfonso Policicchio^c, Teresa J. Bandosz^{c,*}

^a Institute of Combustion Problems, Synthesis of Carbon Nanomaterials in Flame Laboratory, Bogenbai Batyr str., 172, 050012, Almaty, Kazakhstan
 ^b Al-Farabi Kazakh National University, Faculty of Chemistry and Chemical Technology, Department of Chemical Physics and Material Science, Al-Farabi Avenue 71, 050038, Almaty, Kazakhstan

^c Department of Chemistry and Biochemistry, The City College of New York, New York, NY, 10031, USA

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ABSTRACT

Hydrophobic soot was prepared by a simple impregnation of soot particles with cobalt, nickel or iron salts, followed by heat treatment at ~ 800 °C. X-ray and thermal analyses revealed that metal (Co and Ni) or oxide (magnetite) nanoparticles were deposited on the surface of soot particles. The evaluation of the soot microstructure and porosity by Raman spectroscopy, and adsorption of nitrogen, respectively, revealed only small differences between samples. This reflected in the similar amounts of oil adsorbed (more than twice of a soot weight). Nevertheless, even with these small differences, the clear linear correlation between the amount of oil adsorbed and the volume of pore/voids (evaluated by nitrogen adsorption) could be established. The soot with adsorbed oil was easily separated from a water phase. These findings direct the efforts towards optimizing both porosity and magnetic properties of this kind of adsorbents. The results suggested that a deposition of this soot on a fibrous or highly porous supports such as foams or sponges might result in low-cost adsorbents of a high adsorption capacity and an easiness of a mechanical separation after a cleaning process.

1. Introduction

The spills of oils and other industrial chemicals create threats to the environment. They affect not only ecosystems but also human health and have an impact on a regional and global economy. Generally, to remove oil spills physical, chemical or bioremediation methods are used [1]. While the chemical methods based on oil burning and solidification often lead to secondary pollution, the bioremediation suffers of a low efficiency. Therefore, the adsorption of oils by physical forces on sorbents is often considered as an optimal-choice treatment. To effectively adsorb or filter oil from water mixtures porous materials of superhydrophobic and superoleophilic properties are used [1–5]. Those properties are engineered by an introduction of hierarchical micro/ nanostructures that lead to a high degree of a surface roughness resulting in hydrophobicity. Examples are polystyrene fibers [6] or polyester, polyethylene pads, peat moss, clays or vermiculite [1,7–10]. Often the sorbents are modified with hydrophobic coating to increase their affinity to oils. Not without importance are the costs of these materials, of their removal from an oil spill site, and also of a regeneration process.

Carbon-based materials are known for their hydrophobicity [11]. Nevertheless, that degree of hydrophobicity differs between this group of materials and for example activated carbons, which are one of the most porous materials, often reveal a certain degree of hydrophilicity [12]. More hydrophobic than activated carbon is expanded graphite where big pores can attract a significant quantity of oil. Even though these two groups of materials can adsorb a significant quantity of oils [2,13,15,16], their application to oil spills is rather limited owing to the difficulty of their physical separation from a water phase.

Another carbon material which has been explored as an oil adsorbent is soot [1,2,13]. It is formed in an incomplete combustion of hydrocarbons in a simple and cost-effective process. Even though soot is known for its hydrophobicity and it is commonly used in the synthesis of rubber and in a plastic industry, its direct application to remove oil is associated with a significant difficulty of its separation from a water phase. To overcome the separation issue Gao at al. deposited soot in a melamine sponge and used that device to adsorb oil [2]. Their soot had particle sizes between 5-50 nm and a high specific surface area of 440 m^2/g . Its water contact angle was 140°. The resulting melamine sponge with deposited soot of 5-50 nm particles had pores with sizes reaching

* Corresponding author. *E-mail address:* tbandosz@ccny.cuny.edu (T.J. Bandosz).

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Received 9 February 2019; Received in revised form 19 March 2019; Accepted 6 April 2019 Available online 28 April 2019 2213-3437/ © 2019 Elsevier Ltd. All rights reserved. 1 mm and on the average (depending on the kind of oil) it adsorbed 45 g of oil per gram of sponge. The performance of nonmodified melamine sponge was not reported. The amounts of oil adsorbed reported in the literature on other carbon containing sponges or foam (graphene, activated carbon) were between 20 g/g and 150 g/g [2,14–16]. In all cases, the adsorption capacity was exclusively linked to the hydrophobicity of the carbon phase and to the physical/porous form of a sponge. The specific active sites on the surface have rather not been discussed. Such sponges were reported to be easily separated from a water phase and recycled [2,13].

Another way to increase the separation of hydrophobic adsorbent materials from a water phase is an introduction of magnetic properties. This route of the oil removal has been explored by Song at al. who modified polymer fibers with Fe_3O_4 nanoparticles [6]. Their fibrous materials based on polystyrene adsorbed between 65-94 g of oil per g. Since the sorbent was used in the form of a felt, its magnetic properties were not essential to separate the adsorbent from a water phase. Interestingly, the amount adsorbed slightly increased after the introduction of Fe_3O_4 . Magnetic nanoparticles also increased the mechanical properties by increasing the strength of interactions between the fibers. The final content of Fe_3O_4 was not reported but in the preparation procedure 1 g of polystyrene and 0.5 g of Fe_3O_4 were used. The differences in the oil adsorption capacities were linked to the differences in the viscosity of oils and a higher viscosity of oil resulted in a higher amount adsorbed.

The adsorption of oil on a magnetic sponge modified with straw soot has been investigated by Beshkar and coworkers [12]. Their adsorbent was prepared by dipping a polyuretane sponge first in the dispersion of straw soot and then in the dispersion of Fe₃O₄ nanoparticles. The amount of soot on the sponge was 5 wt % and the sizes of Fe₃O₄ nanoparticles were between 20-30 nm. The amount of waste lubricant oil adsorbed was 30 times of a magnetic sponge weight. As in the report by Song et al. [6], the adsorption capacity of the sponge itself was not reported. The information about the content of Fe₃O₄ was also not included.

Based on a recent literature review, on the attractiveness of soot itself as an oil adsorption-enhancing agent, and on an inexpensive soot production technology, the objective of this paper is the analysis of soot of magnetic properties as an oil adsorbent itself. The magnetic soot was prepared using a facile method based on a simple impregnation of soot by metal salts followed by heat treatment. The magnetic properties of the soot addressed here are linked to the presence of either only magnetite [17], or nickel [18,19] or cobalt nanoparticles [20,21]. The latter were formed as a result of a very simple synthesis method. The soot modified in this way has a potential to be used as an inexpensive oil adsorbent itself or as a modifier of sponges, fibers or foams where its magnetic properties can be beneficial for the separation processes. Our aim is to demonstrate that both porosity and magnetic properties of soot are important assets which, when optimized, might lead to the development of efficient oil adsorbents.

2. Experimental

2.1. Materials

Soot addressed in this work was produced during combustion of a propane-air mixture (propane: $50 \text{ cm}^3/\text{min}$; air: $260 \text{ cm}^3/\text{min}$; exposure time: 4 min). The synthesis followed the procedure addressed by Naha et al. [22] with modifications. Flow rate of the combustion mixture was $55 \text{ cm}^3 / \text{min}$. 3 g of soot were dispersed in 1.3 ml of saturated solutions of salts (FeCl₂, CoCl₂, or NiNO₃) and thoroughly mixed for 30 min. After that, the samples were stored at a room temperature (28 °C) for 30 minutes and then dried in an oven at 100 °C for half an hour. In a next step they were placed in a quartz tube of a furnace and heated up to ~ 800 °C in an argon atmosphere for 40 min. Resulting samples are referred to as Ni- Co-, Fe-soot following the metal salts used for

modifications.

2.2. Characterization of materials

The SEM analysis of the obtained samples was carried out on a scanning electron microscope Quanta 200i 3D (FEI, USA) with an EDX AMETEK detector. The accelerating voltage was 15 kV, working distance 15 mm, and accumulation time 100 seconds. Optical micrographs were taken on a DM 6000 M digital materials-science light microscope (Leica Microsystems, Germany) in reflected light mode. The maximum magnification of a dry lens was 1500x with a resolution of about 300 nm. The wetting contact angle was measured using a drop shape analyzer DSA25 KRÜSS GmbH Kruss device for measuring the wetting angle of the material surface. The accuracy of the device is 0.1°. The experiments were done at 25 °C, under 931 MPa and at air humidity 60-80%. Distilled/deionized water was used. A 2 μ L drop of water was dosed on the sample. After 5 seconds of stabilization the wetting angle of the sample surface was measured.

A porosity was evaluated from the measurement of nitrogen adsorption isotherms at $-196\ ^\circ C$ following the IUPAC recommendations [23]. From them, a BET surface area, S_{BET} , total pore volume, V_t (at $p/p_o=0.98)$ and pore size distributions were calculated. For the latter an adsorption branch and BJH method were used. The standard error on nitrogen adsorption isotherms' measurement is less than 5 %.

The XRD experiments were carried out on a Phillips X'Pert X-ray diffractometer (PANalytical, Almelo, The Netherlands). The soot in a powder form was analyzed by CuK_{α} radiation at 40 kV and 40 mA. Thermal analysis was carried out on a SDT Q600 Simultaneous TGA/ DSC Thermal Analyzer (TA Instruments, Newcastle, DE, USA). About 20 mg of soot were heated up to 1000 °C with a heating rate of 10 °C/ min under a constant air flow of 100 mL/min. Based on the residue left after burning the samples at 1000 °C the content of an inorganic matter (metals/oxides) was evaluated. The experiments were also run in helium at the same conditions to evaluate the thermal stability of soot tested. Raman spectra were measured on Solver Spectrum instrument (NT-MDT) using the 473 nm laser on with. The laser beam was directed on the sample using a 100 \times 0.75 NA Mitutovo lenses providing a laser spot $< 2 \,\mu m$ in diameter. All spectra were normalized and the width and intensity of the peaks were analyzed by the Lorentz decomposition using Origin software.

2.3. Oil adsorption test

The amount of oil adsorbed was determined following the method described by Song et al. [6]. Between 0.1 and 2 g of a sorbent were placed on an aluminum foil. Then the crude oil was dripped onto the sorbent by a single-channel of $1000 \,\mu$ l dispenser. When the sorbent appeared as fully saturated, it was drained for 2 min and weighed. The oil adsorption capacity of the sorbent was determined by the following equation:

$q = (m_{ws} - m_s)/m_s$

where q is the adsorption capacity of the sorbent in g/g, m_{ws} is the weight of the sorbent with the adsorbed oil in grams and m_s is the initial weight of the sorbent.

3. Results and Discussion

Since our intention was the synthesis of magnetic soot samples their magnetic properties were evaluated by visual testing of their attraction to a magnet (Fig. 1). As seen, all samples are magnetic and the particles are strongly attracted to the magnet.

The SEM images of the soot are presented in Fig. 2A. Besides small particles of the inorganic phase evenly distributed between small soot particles, large aggregates with sizes of about 1 μ m are also visible. In



Fig. 1. Attraction of the synthesized soot particles to a magnet. Circles indicate the parts of magnets with the soot particles attracted to a magnetic field.

Co-soot this aggregation is the most pronounced.

 Table 1

 Content of elements based on the EDX analysis

In the optical images presented in Fig. 2B the differences in the sizes and distribution of the inorganic phases are clearly seen. In the case of Ni-soot the distribution of the nickel particles is very homogeneous and the particles of the inorganic phase are very small and similar in size to the soot particles. In Co-soot, the inorganic particles (bright in the image) are also homogeneously distributed but they are much larger than those in Ni-soot. The composition of Fe-soot is the most heterogenous and large aggregates of bright spots are easily distinguished with sizes reaching 20 μ m. These differences should be related to the chemistry of the inorganic phase, the particle size and the interaction between the particles leading to the aggregate formation [24,25].

The EDX analysis data is collected in Table 1. Even though there are similarities in the content of oxygen and metals in Fe- and Co-soot, Nisoot is much more oxygen-deficient and contains almost three times more metal than the two other samples do. Thus, this sample is expected to be the most hydrophobic and the results suggest that nickel is mainly in a metallic form. Oxygen can be either bound to nickel or be incorporated to the surface of soot in the form of functional groups [12]. Taking into consideration the difference in the valency of metals, more oxygen on Fe-soot than that on Co-soot can be explained by its involvement in iron oxide with iron on +3 or in a mixed oxidation state. In fact, based on the magnetic properties, Fe₃O₄ is expected to exist in Fe-soot. Nevertheless, the results suggest that still some oxygen

content of cicinents based on the EDX analysis							
Sample	C [at. %]	C [wt. %]	O [at. %]	O [wt. %]	M ^a [at.%]	M ^a [wt.%]	
Fe-soot Co-soot Ni-soot	93.6 94.8 94.1	87.4 88.6 80.9	4.7 3.7 1.8	5.9 4.6 2.1	1.4 1.5 4.1	5.9 6.7 17.1	

^a Specific metal in the sample.

is incorporated to the carbon matrix of soot particles.

More information on the form of metals responsible for the magnetic properties can be derived from X-ray diffraction patterns collected in Fig. 3. In the case of Ni-soot the presence of metallic nickel is confirmed by the diffraction peaks at 44.51 and 51.85 20 [18,19]. Application of Scherrer equation leads to crystalline size of nickel of about 10 nm. Interestingly, in the case of Co-soot, no Co_3O_4 cobalt oxide known for its magnetic properties is detected in the crystalline form and the peaks at 44 and 51 20 [21] represent metallic cobalt of crystalline sizes of about 70 nm. Since the peaks at ~ 41 and ~ 47 20 cannot be linked to cobalt oxide, there is a high probability that they represent Co_xC_y carbides [26]. Both nickel and cobalt nanoparticles have been reported as having magnetic properties [19,20].

In the case of Fe-soot the diffraction peaks at 30.57, 35.89, 43.58, 54.1 and 63.24 20 are a clear indication of magnetic $Fe_{3}O_{4}$ [27]. Its



Fig. 2. A) SEM images on modified soot; B) Optical images of the soot samples.



Fig. 4. Results of thermal analyses in air (A) and in helium (B).

crystalline sizes are about 20 nm. Besides, Fe_2O_3 is also present in this sample and it is represented by the diffraction peaks at 33.3, 41.04, 57.5 and 60.99 20.

Thermal analysis in air provides semiqualitative information about the content of an inorganic phase (Fig. 4A). In all cases the combustion/ decomposition of the carbon phase takes place at about 600 °C and the weight lost pattern for Fe-soot in this temperature range indicates the high chemical homogeneity of the carbon-containing phase of this sample. The thermal behavior of Co- and Ni-soot is more complex than that of Fe-soot. Their DTG curves show numerous sharp peaks representing different processes of a samples' decomposition. They are likely related to the effect of nanoparticles of various sizes on the catalytic gasification of the carbon phase [28,29]. In the case of nickel, a small weight increase at about 400 °C can even suggest the formation of nickel oxide.

The mass left after burning in 1000 °C is expected to represent metal oxides, which were either in the bulk materials or formed during the high temperature oxidation. The results show that the oxide content in Ni-, Co- and Fe-soot is 33 %, 25 %, and 22 %, respectively. A small difference between the iron content from the EDX analysis and TA data for Fe-soot supports the presence of magnetite as the major inorganic phase in this sample. Interestingly, the most marked difference between the EDX results and thermal analysis is found for Ni-soot and Co-soot. Assuming that NiO is present after oxidation, the 35 % mass left might be associated with ~ 27 wt. % nickel, which is much more than detected by EDX (17 wt. %). In the case of Co-soot, assumption that Co₂O₃ is present would lead to 17 wt. % of Co and EDX analyses showed only 6.7 wt. % of Co. These differences might be caused by the

inhomogeneity of the samples' compositions, as seen on the SEM and optical images (Fig. 2).

An effect of Ni and Co nanoparticles on the carbon phase gasification [28,29] is seen on TG curves recorded in helium (Fig. 4B). For both C- and Ni-soot samples a continuous weight loss is recorded after 400 °C even though the oxygen was not supplied to the system. The decomposition of oxygen groups associated with the carbon matrix in Ni-soot is likely seen as an about 1.5 % weight loss at \sim 430 °C and as about 3 % for Co-soot up to 550 °C. These amounts are comparable to those detected by the EDX analysis (Table 1). Interestingly, the total weight loss is 11 % for Ni-soot and 10 % for Co-soot and they occur rather continuously after 600 °C. That trend suggests the gasification of carbon by nanoparticles, although the reduction of some oxides (in small amounts and/or in amorphous forms not detected by XRD) and a removal of oxygen as a CO/CO2 form cannot be ruled out. Taking into consideration the discrepancies in the content of metals between the EDX and TA results, the inhomogeneity of the samples could lead to the underestimation of the oxygen content in the former analysis. In the case of Fe-soot the decrease in the weight loss is more or less consistent with its oxygen content and a sharp decrease in weight after 800 °C, represented by two peaks on DTG curve, is likely related to the reduction of its iron oxides.

Results of Raman spectroscopy confirm the differences in the microstructure of the soot samples caused by the modification with the addition of the magnetic phase. The collected spectra are presented in Fig. 5. The D and G bands are visible at about 1350 cm⁻¹ (deformed sp³ carbon) and 1588 cm⁻¹ (sp² carbon), respectively [30,31]. The intensity ratio of D band to G band (I_D/I_G) is used to analyze the disorder degree



Fig. 5. Raman spectra of the magnetic soot samples studied.

in the carbon structure. The values of I_D/I_G for Ni-, Co- and Fe-soot are 0.88, 0.92 and 0.62, respectively, suggesting that the latter sample has the ordered sp² states. Since the same soot was the bases for the synthesis of all samples, such differences in the defect levels are related to the influence of the magnetic inorganic phase formed during the heat treatment on the "organization levels" of the sp² units in the carbon matrix. In fact, these results are in agreement with the findings of the thermal analysis, which showed the highest level of the chemical homogeneity/least complexity of the carbon matrix. These "complexity levels" reflect the disorder level of the carbon in the soot samples.

Since our intention is to test our magnetic soot samples as oil adsorbents, their surface areas and porosities were evaluated from the nitrogen adsorption isotherms. Their shape and nitrogen uptake show a very low porosity and mainly the presence of mesopores (Fig. 6). The calculated surface areas, $S_{\text{BET}},$ for Ni-, Co- and Fe-soot are 94, 145 and $157 \text{ m}^2/\text{g}$. The similarity of the results for two latter samples is consistent with their similar carbon content (Table 1). More metal in Nisoot decreases the effective surface area of this sample by so-called mass dilution effect caused by providing a heavy metal-based phase. The total volumes of pores do not differ significantly for three tested samples (0.429, 0.390 and 0.401 cm³/g for Ni-, Co- and Fe-soot, respectively). Those large pores are just formed between the aggregated soot particles since soot itself is nonporous. The slightly larger pore volume in Ni-soot (mainly in the range of large mesopores) might be the result of the high content of the nickel nanoparticles. They might form aggregates between which those pores are formed.

For oil adsorption surface hydrophobicity is an important factor. The contact angle measured for Ni-, Co- and Fe-soot was 140.7 $^{\circ}$, 132.2 $^{\circ}$ and 151.4 $^{\circ}$ (Fig. 7), respectively, indicating water repelling properties and the superhydrophobic surface of Fe-soot. A surface roughness can also contribute to these values. Attempts to measure the contact angle for oil droplets failed due to an instant spreading of the droplet on the soot samples.

The results of the crude oil adsorption test are presented in Fig. 8A. The experiments were performed on 6 samples of each soot, with an increment in weight of the soot from 0.1 to 2 g. Crude oil was added up to the saturation of the soot samples. The calculated error bars are included in Fig. 8A and B. As seen, the amount adsorbed on Ni-, Fe- and Co-soot is 2.35 \pm 0.22 g/g, 2.16 \pm 0.26 g/g, and 2.09 \pm 0.35 g/g, respectively and the soot with adsorbed oil can be easy separated from the water phase using a magnetic field (Fig. 9). All samples show the similar oil adsorption behavior with the amount adsorbed within the range of the error bars. Nevertheless, Ni-soot, although not the most hydrophobic, can be considered as the best performing sample and it might be related to its highest volume of the between-particles pores. Taking this into consideration, the dependence of the amount adsorbed on our samples on their volume of pores measured by nitrogen adsorption was plotted (Fig. 8B). Even though not marked differences in the considered quantities exist, an almost perfect linear correlation was found indicating the paramount role of the voids/pores in hydrophobic solids for oil adsorption. Obviously, hydrophobicity is an important asset but to achieve a good performance in oil adsorption this feature must be accompanied by a high porosity.

The amounts adsorbed were smaller than those reported on soot or graphene sponges or foams on which up to 100 g of oil per gram of a hydrophobic foam were reported, as discussed in the Introduction section [2,13,14-17]. Nevertheless, one has to remember that our materials have small surface areas and are not deposited on a foam support providing large pores of the mm size such as sponges [2,13]. The high amounts of adsorbed oil were reported on carbon foam or modified sponges. On these materials, owing to a high volume of millimeter size pores, oil could be stored when attracted by the hydrophobicity of the carbon/sponge phase [2,13-17]. The amounts of oil adsorbed were also reported as being affected by the viscosity of oil and this feature is especially important to keep oil inside of the large sponge pores [13]. In the case of our materials, oil is adsorbed exclusively on the surface of the soot particles and apparently the amount of the magnetic phase or its chemistry does not affect significantly the performance of the adsorbents that is governed by the hydrophobicity of the carbon soot matrix itself. Nevertheless, the magnetic properties of the inorganic phase have a crucial effect on the feasibility of the separation of the adsorbent from water and the choice of this phase would depend on the costs of the process and availability of the resources.

4. Conclusions

The results collected demonstrated that soot obtained in the incomplete combustion of hydrocarbons can be converted into a magnetic hydrophobic material by a simple impregnation with Ni, Co and Fe salts, followed by a high temperature heat treatment. That facile modification route introduced magnetic nanoparticles deposited on the surface of soot particles. They are either metal- (Ni and Co) or oxide (magnetite)-based with sizes in the nanometer range. The treatment only slightly affected the microstructure of the carbon matrix or the



Fig. 6. Nitrogen adsorption isotherms (A) and BJH pore size distributions (B) for the magnetic soot samples.



Fig. 7. Contact angle measurement results for water droplets.



Fig. 8. The comparison of the amount of oil adsorbed in the tested soot with the marked standard deviation (A) and the dependence of the amount of oil adsorbed on the volume of pores/voids (B).



Fig. 9. Visualization of the steps in the oil adsorption testing of magnetic soot and the separation of the spent adsorbent from the water phase using a magnet.

degree of hydrophobicity. The modified soot adsorbed oil in the amounts more than twice higher than its weight. Although the surface hydrophobicity is very important, the results also clearly showed that pores/voids between particles govern the amount of oil adsorbed. Thus, the soot modified in this way and with further optimized surface features, when deposited on other fibrous or porous supports (foams or sponges) has a potential to provide both, a high adsorption capability and easiness of an application/separation in oil-spill cleaning applications.

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